

PREPARATION AND PROPERTIES OF GALLIUM NITRIDE EPITAXIAL LAYERS

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Report III: Lattice parameters measurements of different GaN samples, undoped or doped with Zn or some iron group metals.

Report IV: The influence of doping with Al and some iron group metals on optical and electrical properties of GaN epitaxially grown from the vapor phase.

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PREPARATION AND PROPERTIES OF GALLIUM NITRIDE
EPITAXIAL LAYERS

av

Olle Lagerstedt

fil mag, Kr



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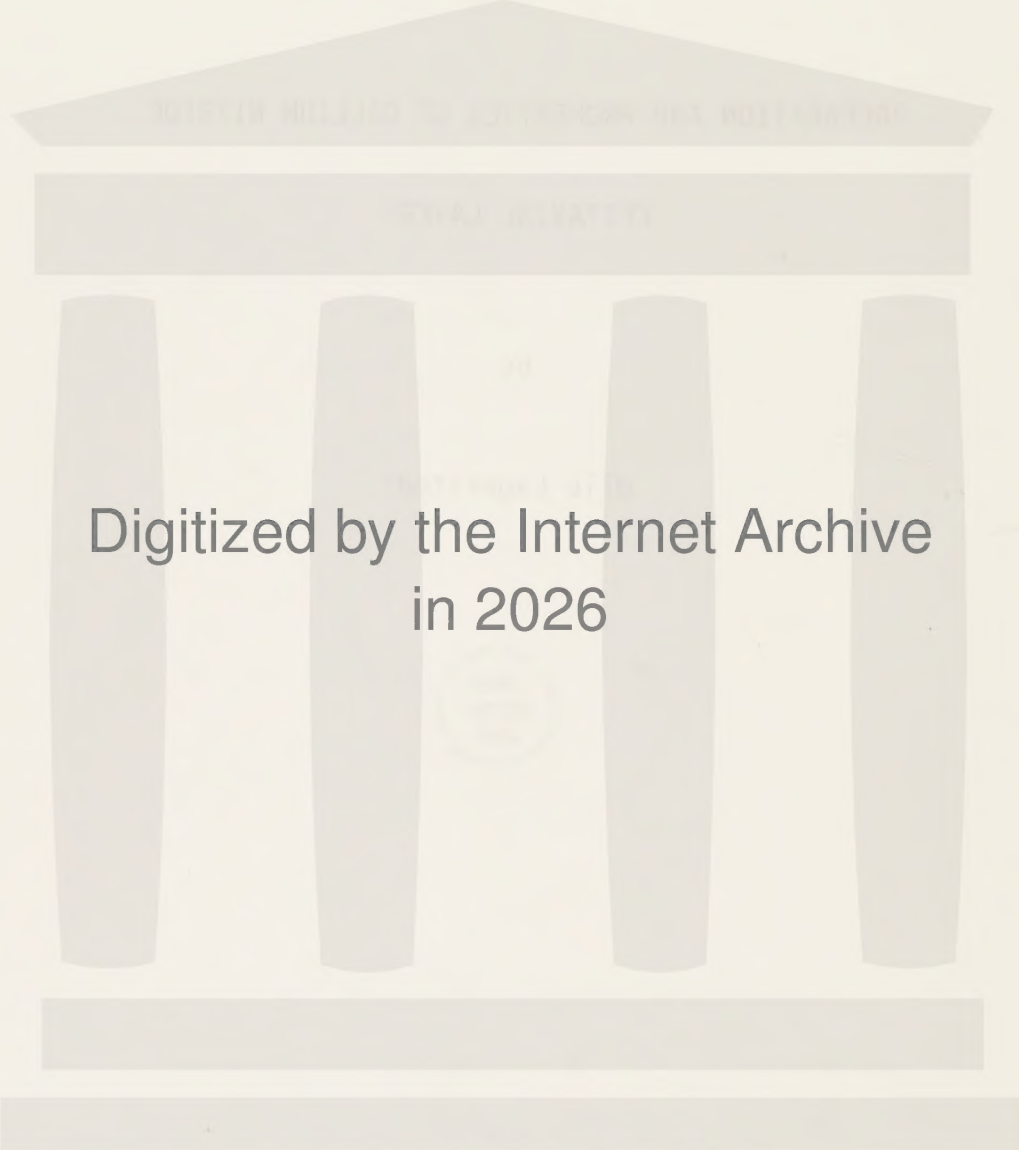
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EPITAXIAL LAYERS

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This thesis is based on the following six reports which in the text will be referred to by their Roman numerals.

- I. Luminescence in epitaxial GaN: Cd, J Appl Phys 45, 2266 (1974)
- II. Properties of GaN tunneling MIS light-emitting diodes, J Appl Phys 49, 2953 (1978)
- III. Variation of lattice parameters in GaN with stoichiometry and doping, Phys Rev (to be published)
- IV. Properties of VPE-grown GaN doped with Al and some iron group metals, Manuscript
- V. Properties of Zn-doped VPE-grown GaN: I Luminescence data in relation to doping conditions, Manuscript
- VI. Properties of Zn-doped VPE-grown GaN: II Optical Cross Sections, Manuscript.

The work in all reports was carried out in collaboration with Dr B Monemar. In reports II, V and VI Civ ing H P Gislason was also a co-author.

Preparation and properties of gallium nitride epitaxial layers

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Introduction

The phenomenon electroluminescence (EL) has fascinated many scientists ever since it was discovered 72 years ago in silicon carbide by H J Round [1]. Electroluminescence means generation of light by the passage of a current in a material under an applied electric field. Although EL strictly implies the emission of visible radiation, it is usually extended to include emission also in other regions of the spectrum. The emitted radiation differs from thermal radiation (Planck radiation) among other things by the relatively narrow wavelength range contained within the spectrum. EL may even be almost perfectly monochromatic, as in the injection laser [2].

An electroluminescent diode or LED (light-emitting diode) is a semiconductor component converting electrical energy into electromagnetic radiation. It is convenient to divide these components into two categories, depending on the spectral region in which the components emit.

I). Sources emitting visible radiation. This category includes the use as indicator lamps, displays in electronic calculators, watches and in many electronic instruments. For these applications the LED's have a number of important properties which make them very attractive.

1). Low power requirement. (A typical device requires 20 mA and 1.7 V.)

2). Reliability and long life. (Typical LED's operate for more

than 10^5 hours.)

3). High luminance. (A typical value 10^4 cd/m².)

4). Small size.

II). Sources emitting infrared radiation. This category includes the use of incoherent sources and injection lasers. The applications of these devices are often qualitatively similar. Most of the applications are in optical communication systems.

In the following only LED's from category I will be discussed.

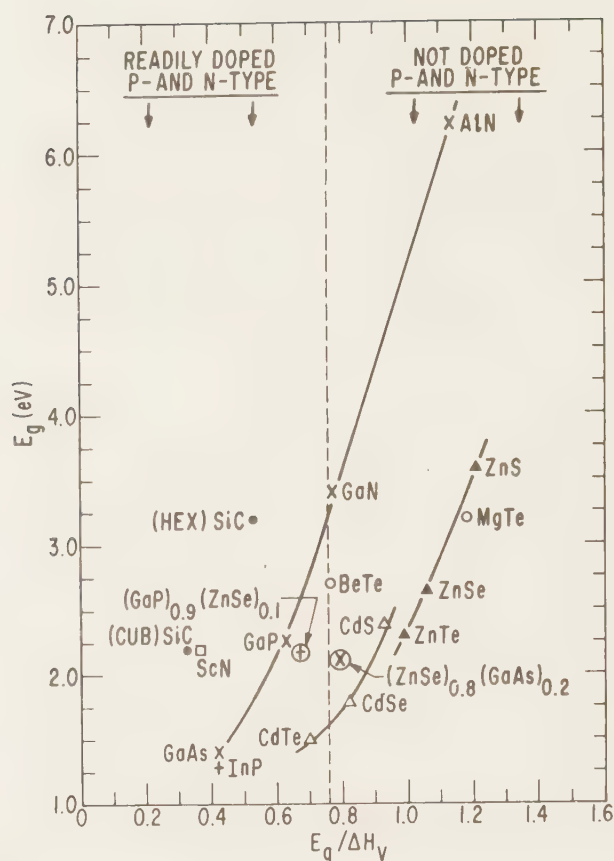
It was rather early established that visible EL from a solid-state LED requires a semiconductor whose band gap energy exceeds 1.8 eV. From this standpoint it is obviously not possible to make LED's in the visible region of the spectrum with the materials Si, Ge or GaAs which are extensively studied and for which technologies have been developed for their application in pn junction devices. The obvious approach to realize such LED's was to find a material that has a direct band gap and a band gap that is sufficiently large to produce visible radiation. Much of the early research on realizing LED's was concentrated on the alloy material gallium arsenide-phosphide ($\text{GaAs}_{1-x}\text{P}_x$) which was considered as a suitable material. In 1968 the first practical $\text{GaAs}_{1-x}\text{P}_x$ numerical display was introduced to the market. This was the result of six years intensive research at two industrial organizations. Beside the research on $\text{GaAs}_{1-x}\text{P}_x$ there has been much attention to the indirect band gap material gallium phosphide. It has been shown possible to overcome, to a large extent, the disadvantages due to the indirect band gap of the material. From these two materials, red, yellow and green emitting LED's can be made, and are commercial available.

After the first discovery of efficient EL in GaAs in 1962 [3], it has been an enormous research on the III-V semiconductor synthesis, single crystal growth, EL phenomena as well as device technology. The successful results have led to a rapid expansive optoelectronic device industry. In 1978 the total LED market in USA, Japan and Western Europe was together 211 milj \$ and is estimated to be doubled in four years. This LED market is about 2.5% of the total semiconductor device market in these countries (8600 milj \$) [4].

As mentioned above commercially available devices are restricted to the wavelengths greater than 5500 Å (2.2 eV). The maximum photon energy is emitted by the green-emitting LED made of GaP:N. It would be desirable to produce light over the entire visible region, i.e. 4000-7000 Å (3.1-1.8 eV). It is however well known that combinations of only three primary colours are necessary to produce every colour that is discriminated for a human eye. This is possible only by focusing the three colours on a spot and vary their relative intensities until the wanted colour is received. These three primary colours are red, green and blue. To produce such a cosmochrome colour generating display system (all colours discriminated for a human eye), one needs a semiconductor with a large band gap ($E_g > 2.6$ eV) and preferably also direct band gap. The realization of that system is strongly related to the possibility to master the technology for a new less studied material. Besides the large band gap this material should also be possible to grow both n- and p-type to form efficient LED's based on injection in pn junctions. The requirement of n- and p-type doping is the most difficult one to satisfy. Almost all data on II-VI compounds and (III-V)-(II-VI) alloys indicate the difficulties to dope these materials both n- and p-type due to compensation by native lattice defects, namely vacancies and/or interstitials [5]. Mandel and Kröger have discussed this problem in terms of a model where a binary semiconductor can be made both n- and p-type if the enthalpy of vacancy formation (ΔH_V) is larger than the band gap energy [6, 7]. In other words, the most promising compounds for both p- and n-doping are those with $E_g/\Delta H_V < 1$. The energy gap for a serie of semiconductors as a function of $E_g/\Delta H_V$ is shown in Fig 1 below. As can be seen in the figure most of the larger direct gap semiconductors are those to the right side of the dashed line. Those to the left side of the line ($E_g/\Delta H_V \approx 0.75$) can rather easily be made both n- and p-type. Recent data on highly refined material indicate that the above crude rule may not exclude the realization of both n- and p-type material even in the case of $E_g/\Delta H_V > 1$ [8].

As seen in Fig 1 the III-V semiconductor GaN has an energy gap above the entire range of the visible spectrum, and is considered as a material with a large potential in realizing a display system for cosmochrome applications [9].

Fig 1. The minimum 300 K energy gap of a serie of semiconductors as a function of energy gap to enthalpy of vacancy formation, taken as half the sublimation energy of the compound [2].



Preparation of the material.

The first report of preparation of GaN was presented in 1932 [10]. The material prepared was a grey polycrystalline powder. This compound was obtained by passing ammonia gas over metallic gallium at high temperatures. The reaction can be expressed as follows:



The temperature on the gallium was 900-1000°C. All attempts to react gallium directly with molecular nitrogen gas failed [10]. The problems in growing GaN can be attributed to the facts that GaN decomposes already at 600°C in vacuum (about 1000°C in one atm pressure of N₂), and that gallium does not react with molecular nitrogen to reform GaN. The melting point of GaN is estimated to be greater than 1700°C [11], where the equilibrium pressure is around 10⁵ atm [12]. These properties explain the problems in the preparation of GaN by the classical techniques. The GaN grown at temperatures above 800°C and at normal

pressure will always be partially dissociated. The difficulties in growing the material have been a limiting factor in obtaining high quality single crystals, and therefore also in research on fundamental properties of the material. Because of this many efforts have been made during the last decade to develop different GaN growth techniques. Some of the most important methods of growing GaN are listed below:

- 1). Reaction of ammonia gas with metallic gallium at temperatures $T > 700^{\circ}\text{C}$ [10].
- 2). Growth of single crystals by heating the grey-white powder (obtained by method no 1 above) at 1100°C in a flow of ammonia. In this way needles with the size of a few mm could be grown in a period of a few days [13].
- 3). Reactive evaporation method, in which pure gallium is deposited onto a substrate in an atmosphere of activated nitrogen gas at a controlled partial pressure [14].
- 4). Liquid phase epitaxy (LPE). Because of the low solubility of GaN in Ga it is not possible to grow GaN with useful crystal dimensions from the liquid phase by cooling of saturated melts. However, in a thermal gradient across the melt, with the partial pressure of NH_3 greater than the equilibrium pressure, dissolved nitrogen is transported to regions of lower temperature, where growth on a substrate occurs. The nucleation is controlled by adding Bi to the growth solution. The growth rate obtained was less than $5\text{ }\mu\text{m/hour}$ [15].
- 5). Growth by a vapor-liquid-solid (VLS) technique ($\text{N}_2, \text{Ga}, \text{GaN}$) on single crystals at high pressure and high temperature. This has been studied between $1000\text{--}1200^{\circ}\text{C}$ under a nitrogen pressure varying from 1500 to 5000 bar. The growth rate was only about $1\text{ }\mu\text{m/day}$ [12].
- 6). Most of the research efforts to receive good quality epitaxial layers have been made by the chemical vapor deposition (CVD) technique. The technique has received this attention because of the availability of many volatile compounds of gallium. There are three basic types of reaction system that can be used in the preparation of single crystals by this technique. They are as follows:
 - a). Pyrolysis of hydrides.
 - b). Reduction of halides.
 - c). Direct chemical reaction between two or more volatile species

that result in the formation of the compound.

Type a) has been used in some laboratories using $\text{GaBr} \cdot 4\text{NH}_3$ [16], $(\text{CH}_3)_3\text{Ga} \cdot \text{NH}_3$ [17], $\text{GaCl}_3 \cdot \text{NH}_3$ [18] or $\text{Ga}(\text{C}_2\text{H}_5)_3 \cdot \text{NH}_3$ [19]. The best results have been obtained through reduction of halides (type b). The transfer reaction system used is an open-tube flow system, originally developed by Tietjen and Amick [20]. It is a well established technique for the preparation of $\text{GaAs}_{1-x}\text{P}_x$. Tietjen et. al have demonstrated that this type of system can be used, with appropriate modifications, for a wide range of III-V compound semiconductors [21, 22]. The first report in the literature using this process for growing GaN was in 1969 [23]. A minor modification of this apparatus was used by us in this work. In this technique hydrogen chloride is passed over a gallium boat (at about 850°C) to produce the volatile gallium chloride.



This GaCl and H_2 are diluted with the carrier gas N_2 and transported to the reaction zone (1050°C), where the gallium chloride meets an ammonia flow and reacts. The deposition equation is as follows:



The ability to grow GaN with this technique depends on the kinetics of the various reactions involved. That is, decomposition reactions of NH_3 and GaN are much slower than the deposition, which results in a net accumulation of GaN on a substrate, even if it is a metastable phase at the temperatures used for growth [III, IV, 22].

This is a hetero-epitaxial growth, i.e. the epitaxial layer and the substrate consist of different materials. The epitaxial growth is critically dependent on the choice of substrate, and at least three properties must generally be considered when judging the suitability of different substrates:

- a). Crystal structure.
- b). Thermal expansion coefficients.
- c). Chemical inertness to the growth environment.

Property c) excludes many attractive materials because of the non-stability in the HCl atmosphere at 1050°C . The different materials used in the CVD process ($\text{GaCl} + \text{NH}_3$) are $\alpha\text{-Al}_2\text{O}_3$ (sapphire) [23], MgAl_2O_4 [24], $\alpha\text{-SiC}$ [25] and $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$ (YAG) [26]. Substrate

materials such as Si, GaAs and GaP have been used in other growth processes of GaN [14, 16]. We have always used the substrate material $\alpha\text{-Al}_2\text{O}_3$. Different orientations can be chosen but the (0001)-orientation gives the smoothest surface of the epitaxial layers [27]. The three abovementioned properties will be shortly discussed below in the case of (0001)-oriented $\alpha\text{-Al}_2\text{O}_3$.

- a). The sapphire has strictly a rhombohedral structure, but can be described in a hexagonal system with the lattice parameters $a = 4.75 \text{ \AA}$ and $c = 13.00 \text{ \AA}$. There is a smaller hexagon with $a = 2.74 \text{ \AA}$ which is rotated 30° compared with the (0001)-basal plan hexagon. The lattice constant for GaN is $a = 3.19 \text{ \AA}$ [III]. This will give a lattice mismatch of 14%. Due to this large lattice mismatch there exists a very high misfit dislocation density in the first few μm of growth [III, IV].
- b). The thermal expansion coefficient for the a-parameter is $(5.17 \pm 0.05) \cdot 10^{-6} (\text{^\circ C})^{-1}$ for GaN [28] and $7.28 \cdot 10^{-6} (\text{^\circ C})^{-1}$ for the sapphire [29]. Due to this difference, large stresses are built up in the samples as they are cooled down from the growth temperature. The sapphire shrinks more than the gallium nitride. When the layers are thicker than about $50 \mu\text{m}$ cracks will be created in a $250 \mu\text{m}$ thick sapphire substrate and this will be fractioned into many pieces which are hold together by the GaN layer. When the layers are thinner than about $50 \mu\text{m}$, the cracks will instead be created in the GaN.
- c). Sapphire can be considered as a chemically rather resistant material in the atmosphere of GaN CVD growth. Some severe etching of the $\alpha\text{-Al}_2\text{O}_3$ by HCl is however reported in the literature [30]. Sapphire is far from an ideal substrate material for the GaN epitaxial growth because the material and GaN do not have the same crystal structure, lattice constants and thermal coefficients of expansion. Nevertheless it is the best substrate material that has been used so far in the CVD growth of GaN.

Doping.

Since undoped GaN is always n-type, the most interesting dopants are those giving acceptors in the material. The first reported studies of doping GaN were carried out on powder, doped with Li, Zn or Mg [31]. The dopant was incorporated in the material by adding it to the gallium

source before growth. The diffusion coefficients of dopants in GaN in temperatures where GaN is stable are low [32], so doping is normally carried out by including the impurities in the source chemicals of the growth. In an open-tube flow CVD system the dopant is added to the system at a controlled vapor pressure by a separately heated extra side arm or by placing it directly in a boat upstream the growth zone. Dopants with insufficient vapor pressure can be transported to the reaction zone in the form of their chlorides. Silicon and phosphorus are introduced in the form of their hydrides (SiH_4 and PH_3). Dopants known to affect the optical and/or electrical properties of GaN are listed below. Of these dopants, zinc has received the most attention because of its capability to compensate the material and emit blue, green, yellow and red electroluminescence.

Zn [V, VI], Li [33], Cd [I], Mg [34], Al [IV], Fe and Cr [IV], Ge [35], Be [33], Hg [37], P [36], Ca [38], As [38] and Ag [38].

The last four dopants were incorporated by ion-implantation only.

Electrical properties.

Undoped GaN is always n-type, with a carrier concentration around 10^{18} cm^{-3} and mobilities about $100 \text{ cm}^2/\text{V-sec}$. This high electron concentration is probably due to decomposition of GaN during growth, i.e. there always exists a high N-vacancy concentration in samples, giving the shallow donor with the binding energy of about 30 meV which is causing the high conductivity [I, III, 23]. The values of n and μ are very sensitive to the position of the substrate in the growth zone. The lowest values are obtained at the position where GaCl and NH_3 first mix (see Fig. 5 in report V) and further downstream the carrier concentration is increased. This is consistent with the idea that the native donors are N-vacancies rather than unintentionally incorporated impurities during growth. One can not rule out the possibility that Ga-interstitials could also give the high electron concentration but it is less probable [III]. The lowest values reported for undoped GaN have been $n = 2 \cdot 10^{17} \text{ cm}^{-3}$ and $\mu = 380 \text{ cm}^2/\text{V-sec}$ [39]. By doping with different elements (Zn, Mg, Li (Fe, Cr) or Be) the material can be compensated, it becomes semi-insulating. Up to date low ohmic p-type material has not been obtained in single crystalline form. Polycrystalline p-type material with $p = 10^{17} \text{ cm}^{-3}$ and $\mu = 3 \text{ cm}^2/\text{V-sec}$ has

been reported, but these first results need confirmation [12].

Optical properties.

The band gap of GaN was estimated from early absorption measurements. The first measurement of its value was performed on powder material by Kauer and Rabenau. They estimated the band gap to 3.25 eV at room temperature [40]. Later on when large single crystals were available the absorption measurements by Maruska and Tietjen gave the value of $E_g = 3.39$ eV. From this measurement of the absorption it was also concluded that GaN is a direct gap material [23]. Camphausen and Connell studied the temperature dependence of the absorption edge and deduced a value for the temperature dependence of the band gap [41]. Some years ago a more accurate determination of the temperature dependence was carried out by studying photoluminescence excitation spectra, leading to an approximate expression :

$$E_g = 3.503 + \frac{5.08 \cdot 10^{-4} \cdot T^2}{T - 996} \text{ eV for } T < 295 \text{ K} \quad [42].$$

This will give the values $E_g = 3.503$ eV at 1.6 K and $E_g = 3.440$ eV at room temperature.

The reflection spectra of GaN have been reported in a wide range of photon energies. The purpose of these investigations was to reveal the details of the band structure, determine the energy gaps between high-symmetry points in the Brillouin zone [43] and to get some parameters, such as the refractive index [44], effective Born charge and permittivity [45].

In addition to the studies of the absorption and reflection of GaN, various photoluminescence (PL) studies have been reported. From PL spectra of undoped samples a great number of radiative transitions can be identified, such as those due to free excitons , excitons bound to neutral donors, excitons bound to neutral acceptors, donor-acceptor (DA) pair transitions and phonon replicas of the abovementioned transitions [I]. From the PL measurements in report I the donor binding energy is estimated to be $E_d = 29 \pm 6$ meV. The binding energy for the most common shallow acceptor is also determined $E_a = 225 \pm 10$ meV. The origin of the donor and the acceptor is discussed in reports I, II, IV and V. The exciton binding energies are also calculated in report I. There have also been reported luminescence studies on samples intentionally doped

with acceptors. Such dopants give rather deep levels in the material. The shallowest identified acceptor binding energy is caused by Mg and is about 0.3 eV. The position of the PL emissions due to known impurities are listed below

Peak position (eV)	Impurity	Ref.
2.93	Mg	[34]
2.9	Hg	[37]
2.87	Zn	[V, VI]
2.85	P	[36]
2.72	Cd	[I]
2.6	Zn	[V, VI]
2.58	As	[38]
2.50	Ca	[38]
2.43	Hg	[37]
2.23	Li	[33]
2.2	Zn	[V, VI]
2.16	Be	[33]
1.8	Zn	[V, VI]
1.52	Ag	[38]

Studies of infrared quenching of the PL have made it possible to determine the positions of the acceptor levels resulting from doping with Zn, Hg and Li. From these measurements the location of the levels are determined to be 0.45 eV (Zn), 0.41 eV (Hg) and 0.75 eV (Li) above the valance band [37].

Luminescence spectra due to the rather deep acceptor levels are usually broad due to rather strong phonon coupling, which makes the evaluation of binding energy from optical spectra more delicate [V]. A detailed spectral study of the four Zn-emissions is reported in V and VI, yielding the approximate level positions and phonon coupling parameters.

Electroluminescence.

The most efficient LED's require pn-junctions. As GaN so far could only be obtained n-type other possibilities of realizing an efficient LED have to be considered. The EL of GaN was first observed in 1971 by researchers at the RCA [46]. In a partly compensated layer blue EL was obtained at room temperature by passing a dc current between two point contacts. The emission had a rather low efficiency and occurred at many

microscopic spots correlated with grain boundaries [46]. A more well-defined structure was the m-i-n (metall-insulator-n-type) which was presented the same year [47]. This structure consists of a thin insulating Zn-doped layer grown on an undoped layer. Two ohmic indium contacts were made, one on top of the i-layer and one to the edge of the n-layer. From this device, blue to red emission could be obtained dependent on growth conditions and applied voltage. The light appeared at the m-i or at the i-n interface dependent on the polarity of the bias. In some reported cases EL was obtained only in the forward direction [48, 49]. The best reported value of power efficiency is 0.1% and external quantum efficiency 1.1%. These results are obtained for LED's emitting blue-green light [50]. This type of structure made of GaN has been studied in many laboratories, such as RCA (USA) [50], Stanford University (USA) [34], L.E.P Limeil-Brevannes (France) [48], Hitachi (Japan) [49], Siemens (Germany) and at the department here in Lund.

Different injection mechanisms have been suggested. The following model was presented by Pankove and Lampert [50]. As the $I(V)$ characteristic followed Fowler-Nordheim expression $I \sim V \cdot \exp(-b/\sqrt{V})$ the tunneling model was proposed. The high fields required to yield the observed tunneling currents have their origin in partial localization of the applied voltage at numerous sharp points and ridges at the growth interfaces. Under forward bias the electrons tunnel through the barrier at the n-i transition and become hot electrons which can loose their energy by colliding with a Zn-center and cause impact excitation of the luminescent centers. This process explains the observation of EL either at the n-i or at the i-n interfaces, dependent on the polarity of the applied voltage. Pankove has also obtained blue EL in m-i-n structures when the applied dc bias was lower than the energy of the emitted photons. Blue light (emission peak at 2.9 eV) was emitted when the dc bias exceeded 2.1 V. The model proposed was ionization of the Zn center through simultaneous impact excitation by two hot electrons [51]. Jacob and Bois have also reported LED's emitting from blue to orange under applied voltages of about 4-10 V. The highest external quantum efficiencies obtained have been estimated to be 0.5-1%. They only obtained EL with forward bias. The model to explain the injection in the structure involves impurity band conduction and electron injection from the n to the i side. The $I(V)$ characteristic was found to follow the

Frenkel-Poole law [48].

A general problem with m-i-n structures is the fact that the luminescence efficiency seems to drop in compensated material (Zn doped) compared with less compensated. The applied voltages for the reported m-i-n structures were normally between 5-20 V. A LED emitting blue or UV EL with a bias of about 2-3 V is reported in II. The basic working principle of such a LED is a tunneling injection of minority carriers into low ohmic GaN through a thin insulator [II]. The quantum efficiency obtained so far for such a structure was quite low, however [II].

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Variation of lattice parameters in GaN with stoichiometry and doping

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Abstract

Lattice parameters were measured for different GaN samples, undoped as well as doped with Zn or some iron group metals. Very large variations in values of a and c were obtained, the difference between extreme values being as large as 1 %. It appears as nitrogen vacancies V_N cause a decrease in lattice parameters of GaN approximately according to $\frac{\Delta a}{a} \approx \frac{\Delta c}{c} \approx - \frac{V_N}{N_{\text{GaN}}}$. An additional increase in lattice parameters at high growth rates is interpreted as due to selfinterstitials in undoped materials. High doping with Zn and some iron group metals (Fe, Cr, Ni) also causes a large increase of lattice parameters, possibly due to a substantial incorporation of these elements at interstitial sites and at N sites.

I. Introduction

The lattice parameters of a solid material are experimentally easily accessible quantities. They are also fundamental properties of the material, since a great many physical properties depend parametrically on the lattice constants in a simple way. The defect concentration is perhaps the most important factor in determining the transport properties of a semiconducting material. Therefore, it seems surprising that the relationship between defect concentration (including point defects, such as vacancies or interstitials, complexes involving more than one lattice site, or extended defects such as dislocations) and lattice parameters has only received some scattered attention in literature. At present there seems to be no firm theory to predict the influence of such defects on lattice parameters. Quite contradictory such predictions exist e.g. on the influence of vacancies on lattice parameters of semiconductors [1-4]. The experimental situation seems to be equally confusing. It is easy to find even a difference in sign of the change in lattice parameters from different experiments performed on different samples due to a nominally similar introduction of defects in the material [5-7]. It seems clear that more work in theory as well as experiment will be necessary to get a reasonable picture of this important area of defect properties.

The lattice parameters for the wurtzite III-V compound GaN have been investigated previously by a large number of authors, using material grown by different techniques. A remarkably large scatter in values has been reported, with a -values ranging from 3.160 Å to 3.190 Å and c -values from 5.125 Å to 5.190 Å for nominally undoped material [8-28]. A synopsis of such previous data is given in Table I. This scatter in

data is much larger than the accuracy of determination involved in at least a major portion of these investigations. It is therefore reasonable to assume, that the scatter in lattice parameter data for GaN evident from Table I is mainly due to differences in growth conditions and, consequently, in defect concentration. To verify this assumption, and to get some insight into the mechanisms underlying this surprisingly large scatter, we have undertaken a comparative study of lattice parameters for a large number of GaN samples, undoped as well as doped, and grown under varying conditions.

In Sec. II will be described growth and relevant properties of the GaN material used in our experimental study, as well as the procedure of measuring lattice parameters of the samples. Experimental results for lattice parameters of undoped and doped samples are presented in Sec. III. In Sec. IV the obtained results are discussed in more detail and connected with the defect properties of the GaN material used. A comparison is also made with previous results on variation of lattice parameters with defect concentration for other semiconductors. The most important conclusions from this work are listed in Sec. V.

II. Materials and experimental procedure

The material used for this investigation was grown by vapor phase epitaxy on (0001) sapphire substrates, as described separately [29-30]. The deposition temperature was kept at 1025 - 1050 °C, and growth rates (of layer thickness) were varied from very low values up to as

much as 10 $\mu\text{m}/\text{min}$. This was achieved by controlling gas flow rates and the position of the substrate in the deposition zone. Dopants were incorporated during growth by vapor transport. Most GaN layers referred to in this paper had a thickness of about 100 μm . This was necessary to ensure good quality GaN material, since particularly at high growth rates a large defect (dislocation) concentration can occur in the region close to the substrate, sometimes extending as much as about 5 μm away from the substrate (Fig. 1). The preparation of samples for x-ray investigations had to include a polishing step to remove the entire sapphire substrate. In addition the part of the GaN-layer closest to the substrate was removed to leave only GaN samples of proper crystalline perfection for x-ray investigations. These samples were finally ground to powder prior to lattice parameter measurements.

Crystallographic investigations were performed with a Guinier camera. To get an accurate determination of a- and c-values for the GaN unit cell, filtered monochromatic $\text{Cu}_{\text{K}\alpha 1}$ -radiation was employed. Further, a KCl-reference was mixed with the GaN sample. A very accurate densitometer evaluation technique for determination of line positions on the film (normally used for spectroscopic purposes) was available, which allowed good precision in computer evaluated data for a- and c-parameters.

III. Experimental results on lattice parameters

Results from our measurements from 15 different GaN samples are shown in Table II. Two groups of samples were studied. U1-U5 are nominally undoped samples, which should be representative for an evaluation of variation of lattice parameters from growth conditions alone. A second group of samples D1-D7 are doped with iron group metals such as Fe, Cr, Ni, and Cu. Such dopants cause deep levels in the band gap, which are found to affect electrical compensation of GaN [30]. Their possible additional effect on lattice parameters should emerge from the data in Table II. The last group of samples D8-D10 are Zn-doped, and are included to show the effect of rather high Zn-concentrations on GaN lattice parameters.

The data from the group of undoped samples in Table II indicate that variations in growth conditions have a quite remarkable influence on lattice parameters for GaN. Samples U1-U3 represent good quality layers, about 100 μm thick, with carrier concentrations below 10^{19} cm^{-3} (300 K) and mobility about $100 \text{ cm}^2/\text{V sec}$ (300 K). The total detected impurity concentrations in these layers were found to be less than 50 ppm (if rather large amounts of Al normally incorporated in concentrations 100 - 1000 ppm are disregarded) [31], from an analysis with secondary ion mass spectrometry (SIMS). (Some crystals were found to have an impurity content much lower than these stated maximum values.) It is evident from Table II, that such samples show no significant scatter in a -values. There is, however, some variation in c -values for these layers, which indicates a layer sensitivity of c -values for crystal growth parameters. Such behaviour has previously been observed for ZnO [32]. Samples U4 and U5 represent extreme growth

conditions. U4 was grown very rapidly (growth rate about $10\text{ }\mu\text{m/min}$ compared to about $1\text{ }\mu\text{m/min}$ for samples U1-U3) and was found to have a bad crystalline perfection (polycrystalline, high dislocation density). Sample U5 on the other hand was a layer grown very slowly (at a rate $< 0.1\text{ }\mu\text{m/min}$). Such layers have a very good crystalline perfection, as shown by recent channeling studies [33]. Their N-vacancy concentration appears to be very high, however, which makes them degenerate n-type if undoped (the N-vacancy is a shallow donor in GaN [11]). It thus appears as a high growth rate induces large values for the lattice parameters, while consequently low growth rates give low values for both a and c . The difference between our extreme values (U4 vs U5) is about 1 %, which is at least an order of magnitude larger than the largest corresponding shifts reported in GaAs [7].

Our observations on the influence of growth rate on lattice parameters for undoped VPE-grown GaN material are in agreement with the trend that can be observed in the collection of data from previous investigations presented in Table I above. The lowest values for lattice parameters in Table I are for samples grown as powder, where normally very slow growth rates (say $< 0.1\text{ }\mu\text{m/min}$) are obtained.

No systematic study of the influence of doping on lattice parameters of GaN was carried out, since inadvertent contaminants are still a problem in the present technique of GaN VPE-growth. Since iron-group transition metals were found to have interesting effects on the electronic properties of the material [30], we have included material doped with iron-group metals in our analysis of lattice parameters. The results are shown by the second group D1-D7 in Table II. The

samples D1-D3, D6 and D7 in this group are grown with a growth rate about $1 \mu\text{m}/\text{min}$, i.e. about the same as for U1-U3 described above. Comparing these sets of data it seems evident that these iron group contaminants cause a lattice dilation in GaN. A SIMS analysis shows that the main contaminants in the crystals D1-D3, D6 and D7 were Fe and Cr, both present to a concentration of 20 - 100 ppm. Al was present in concentrations 500 - 1500 ppm, which should have a negligible effect on lattice parameters if Al is incorporated on Ga site. (Note that the lattice parameters of GaN and AlN are very similar [22].) Sample D4 has a similar doping, but is grown with a growth rate of about $10 \mu\text{m}/\text{min}$, i.e. similar to U4. The extremely high values for a and c observed for D4 are therefore due to an excessive growth rate in addition to doping. Sample D5 is a crystal grown at normal growth rate ($\approx 1 \mu\text{m}/\text{min}$), but intentionally doped with a high Ni-concentration. The data obtained for D5 (Table II) show that Ni behaves similarly to Cr and Fe in dilating the GaN lattice.

Zn-doping has been employed for the purpose of preparing high-ohmic GaN for light emitting devices [34], and is of great interest because of the different electronic levels caused by Zn in GaN, making light emission over the entire visible spectrum possible [35-37]. Sample D8 is a Zn-doped layer grown rather slowly ($\approx 0.1 \mu\text{m}/\text{min}$) with a rather high crystalline perfection. The lattice parameters of D8 clearly exceeds the corresponding values for undoped material, which means that Zn-doping expands the GaN lattice. The same conclusion is drawn from the results of D9 and D10. These layers were so called in-structures, i.e. a Zn-doped layer was grown on top of a nominally undoped GaN layer, all with a growth rate about $1 \mu\text{m}/\text{min}$. The values

shown in Table II are obtained as an average over the broadened double lines observed in these cases. Indeed if Zn-doping causes an increase in lattice parameters, a double line would be expected to occur in a composite sample as D9 and D10, where undoped material is also admixed. In Fig. 2 is shown an example of such a double line. If the two sets of lines are evaluated separately, we obtain e.g. for sample D10 values $a = 3.190 \text{ \AA}$ and $a_{\text{Zn}} = 3.197 \text{ \AA}$ for undoped and Zn-doped material respectively. The value $a = 3.190 \text{ \AA}$ is typical for rather rapidly grown undoped material (cf. U1 - U3 above). Incorporation of about 10^{20} cm^{-3} Zn therefore seems to cause an increase in lattice parameters of about 0.2 %.

The possible variation of lattice parameters within a particular sample can be judged from the linewidths observed on the films. Except for D9 and D10 discussed above, very narrow lines were observed in all cases (Fig. 2). This means that such variations over the sample were small; the area of the layer used for each sample was also rather small, $5 - 10 \text{ mm}^2$. The fact that the lattice constants are very well-defined within a sample, together with the large variations observed between different samples (which will be shown below to be systematic in defect concentration), is a good argument that the large variations in lattice parameters are indeed created during growth of the material, and not due to strains or dislocations created during the sample preparation after growth (such as the grinding step). Even though the grown in dislocation density well away from the substrate (see above) could still be of the order 10^5 cm^{-2} [18], we again think the narrow line widths give a good argument that possible variations in dislocation density of the layers do not contribute the major effect

(of the order 1 %) on the variation of lattice parameters shown above.

IV. Discussion

To our knowledge variations of room temperature lattice parameters of the magnitude of 1 % was previously unheard of for semiconductor materials. Usually such variations, as reported for the most common semiconductors such as Ge, Si, and GaAs are less than 10^{-4} and typically a few ppm [5, 38-42]. Similar accurate investigations for the more exotic III-V compounds or II-VI compounds seem to be absent, but there is certainly some scatter in published data also for such materials [43, 44], although not as large as demonstrated here for GaN. Our data clearly demonstrate, that accurate evaluation of crystallographic data has to consider the defect properties of the particular sample under study. Sizeable variations seem to occur with growth conditions for undoped material, which is therefore interpreted as an influence of native defects, such as vacancies. Doping with Zn and iron group impurity atoms was also found to influence the lattice constants quite drastically for GaN. We will discuss these "intrinsic" and "extrinsic" influence on lattice parameters in somewhat more detail below.

It has previously been established, that the conductivity of not intentionally doped GaN prepared in the manner described above is generally not due to the incorporated impurities, but rather to the creation of native defects [11, 29]. The material has a tendency to

become low resistive n-type, with an electron concentration far above detected levels for impurities [11]. The most obvious candidate for a shallow donor state causing these effects is the nitrogen vacancy V_N . V_N is expected to behave as a donor in GaN, just as V_{Ga} should be an acceptor [45]. (A corresponding situation seems to have been experimentally proved for GaAs, where V_{Ga} is an acceptor and V_{As} a donor [46].) Furthermore, other intrinsic defects such as antisite defects are calculated to have much higher energies of formation in GaN than the single vacancies, and the latter would therefore be expected to be the important species even after cool-down to room temperature [45]. Therefore we have confidence in the assumption that the n-type conductivity of undoped GaN is due to the isolated V_N donors, which seem to have a shallow binding energy of about 30 meV [29, 47].

Independent of the data reported here we have observed a definite correlation between the growth rate of the epitaxial GaN layers and their electron concentration. Very slowly grown ($< 0.1 \mu\text{m}/\text{min}$) layers always come out degenerate n-type if undoped, with electron concentration (300 K) of typically $5 \cdot 10^{19} - 10^{20} \text{ cm}^{-3}$. A higher growth rate always reduced the electron concentration n ; a rate of about $1 \mu\text{m}/\text{min}$ at 1050°C was found to reduce n well below 10^{19} cm^{-3} at 300 K for undoped layers. This is consistent with previous data taken over a very limited range of growth rates [11]. (With acceptor doping with e.g. Zn, high-resistive material can easily be obtained even for low growth rates [29, 48].) At low growth rate a high V_N concentration is apparently created in undoped material grown at about 1050°C . This is not surprising in view of our present knowledge about the thermal

instability of GaN. In some previous investigations thermal instability has been reported for temperatures as low as 800 °C [49]. Our results further indicate that (for growth rates below 1 µm/min) the more rapid the growth is taking place, the larger is the difference between deposition and dissociation rates, which results in a reduced V_N concentration.

Our data on lattice parameters for undoped GaN reported here establish the relation between growth rates and values of a and c . The above discussion strongly indicates, that the physical correlation involved is the one between lattice parameters and V_N -concentration. Our interpretation is that a large V_N -concentration, say of the order 10^{20} cm^{-3} , corresponding to a very low growth rate ($< 0.1 \text{ µm/min}$) has the remarkable property to reduce the lattice constant more than 0.5 % below the value typical for layers grown at about 1 µm/min, where V_N is estimated to be less than $5 \cdot 10^{18} \text{ cm}^{-3}$. From early measurements on nonstoichiometric GaAs a similar variation of lattice parameters on V_{As} -concentration was claimed [7]. In their case a relation $\frac{\Delta a}{a} \approx \frac{V_{As}}{N_{GaAs}}$ was found to hold up to $\frac{\Delta a}{a} \approx 10^{-4}$, at higher V_{As} -concentration a saturation in $\frac{\Delta a}{a}$ occurred [7]. Note that for GaAs an increase $\frac{\Delta a}{a}$ with V_{As} -concentration was claimed [7]. In our case with GaN we find a decrease in a and c with V_N -concentration, approximately $\frac{\Delta a}{a} \left(= \frac{\Delta c}{c} \right) = - \frac{V_N}{N_{GaN}}$. This is the result obtained from the empirical Vegard's law arguments [50], generally used in the discussion of the influence of point defects on lattice parameters. If we put $\frac{\Delta a}{a} = \frac{4}{\sqrt{3}} \cdot \frac{\Delta r}{a} \cdot \frac{V_N}{N_{GaN}}$, where Δr is taken as an appropriate N-radius in GaN (estimated as an average of covalent and ionic contributions [51]), we obtain $\frac{\Delta a}{a} \approx - \frac{V_N}{N_{GaN}}$.

Unfortunately the crude estimates from Vegard's law seem to be of little value when it comes down to the detailed physical mechanisms involved. The major problem is that there are good theoretical arguments for a rearrangement of bonds at a vacancy so as to produce an outward relaxation of the lattice at a vacancy [45, 52]. At first sight this would imply that all vacancies expand the lattice, which would fit some experimental data on V_{As} in GaAs [7], but is in contradiction to our data on V_N in GaN. Our results would indicate that either there is an inward relaxation around V_N in GaN or there are long range strain fields around such a vacancy, causing a substantial net contraction of the lattice. Further theoretical work is needed to resolve which of these possibilities is correct.

The upward deviation from the "normal" values for the GaN lattice parameters (as represented by e.g. $U1 - U3$ in Table II) are also very large. Such deviations occur for undoped samples grown at a very high growth rate, but also for samples doped with some iron group metals, Zn and Mg [18]. For the undoped samples it is reasonable to assume that a large concentration of selfinterstitials could be created. Independent experimental support for such an argument is given by recent channeling experiments on VPE GaN [33]. It was found that for crystals grown at a very low growth rate, a high crystalline perfection is obtained. This means that the concentration of interstitials is low (the channeling method does not detect vacancies). For crystals grown at higher growth rate, a higher concentration of atoms at interstitial sites was always detected [33]. The notion that interstitials would have a tendency to increase the lattice parameters seems to be generally accepted, and appears to be a very reasonable

assumption. No quantitative estimates of concentrations of interstitials in the sample U5 (and D5) relevant for this discussion can be made at present.

The problem of predicting the influence of doping with foreign atoms on lattice parameters seems to be a controversial one, and quite contradictory suggestions appear in literature. The most general idea is the one of atomic size, based on Vegard's law, predicting lattice dilation if the (covalent) radius of the impurity atom is larger than the one it replaces [50]. In partly ionic materials, such as III-V compounds, additional factors have been proposed to influence lattice parameters, such as effective charge compensation ratio [53]. On the latter case, however, there seems to be a controversy of sign for this contribution in GaAs [53]. In our case of iron group metals as well as group IIB metals, an introduction of these on Ga sites would cause a reduction of the lattice parameters according to Vegard's law, since their atomic radius (covalent as well as ionic radius) are smaller than for Ga. This is contrary to the observations reported here. Ionic charge effects could well be important in the case of GaN, but as noted above no firm predictions seem possible in this case [53]. For group IIB metals previous independent data on electrical properties of Zn-doped GaN have lead to the suggestion that Zn predominantly occupies vacant N sites when introduced in large concentrations [54]. This would be consistent with the above data on lattice parameters, since the simple size arguments predict a lattice dilation when Zn enters N sites. A similar explanation of our data for the iron group metals (Fe, Cr and Ni) studied here can be offered if they preferentially occupy nitrogen sites (i.e. they fill out

N-vacancies). This would also explain the ability of these metal impurities to effectively compensate the V_N donors in GaN to make the material high resistive [30].

In spite of the large variations of a and c between different samples grown under different conditions, the c/a ratio was found to vary much less, within the limits 1.6264 ± 0.0015 as evidenced from Table II and Fig. 3. This can be interpreted as a strong stability of the GaN wurtzite structure against variations in defect concentrations and variations in growth conditions. The stability of the wurtzite structure of GaN can be related to the deviation of c/a from the ideal value 1.633 [55]. We have never observed cubic GaN in our growth of several hundred GaN epitaxial layers, the same conclusion comes from a parallel investigation of freely nucleated GaN single crystals [15]. Cubic GaN has been reported in literature [56], but this observation has apparently not been reconfirmed.

V. Conclusions

Accurate measurements of lattice parameters a and c for wurtzite GaN epitaxial layers reveal surprisingly large variations with stoichiometry as well as with doping with group IIB and iron group metals. Undoped layers grown slowly ($< 0.1 \mu\text{m}/\text{min}$) at 1050°C are degenerate n-type due to a large concentration V_N of N-vacancies. This leads to a drastic reduction in lattice parameters, approximately according to $\Delta a/a \approx \Delta c/c \approx -V_N/N_{\text{GaN}}$. Very high growth rates at 1050°C leads to

increased values for a and c , partly due to a reduction in V_N , but at high growth rates also due to an increased concentration of self-interstitials. Variations in a and c obtained with undoped layers are therefore found to be in excess of 1 %, at varying growth conditions.

Doping with Zn leads to an increase of a and c , such that 10^{20} cm^{-3} Zn atoms causes a lattice dilation of about 0.2 %. This dilational effect is not entirely due to an incorporation at interstitial sites, but also to a large extent into N sites. Doping with Fe, Cr, or Ni in concentrations $2 \cdot 10^{18} - 10^{19} \text{ cm}^{-3}$ causes lattice dilation of the order 0.1 %. The simple Vegard's law arguments imply that the major part of these elements cannot be incorporated on Ga sites.

The collection of data obtained here exhibit a moderate variation of the c/a ratio within the limits 1.6264 ± 0.0015 . This is well below the ideal c/a ratio 1.633, indicating a strong stability of the GaN wurtzite structure, even with drastic variations in defect properties. Cubic GaN would therefore not be expected to form under these growth conditions (1025 - 1050 °C, normal pressure, i.e. far below equilibrium pressure).

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Figure Captions

- Fig. 1 SEM cathodoluminescence topograph of a cleaved edge of an undoped GaN layer (1a), compared to the corresponding SEM surface picture (1b). Within a few μm of the substrate the GaN material has a high defect density, and therefore shows very low luminescence intensity.
- Fig. 2 Comparison between the appearance of diffraction lines on the film for two different samples (D5 and D10). D5 is a homogenous layer, while D10 is an in-structure with Zn-doped GaN on top of nominally undoped GaN. D10 shows a double line interpreted as due to an increase of lattice parameters in the Zn-doped part of the layer.
- Fig. 3 Synopsis of lattice parameters c and a for all investigated samples of GaN. Undoped samples are denoted (o), Zn-doped samples (∇), and iron group metal doped samples (x). The two full lines (—) correspond to the extremal c/a -values observed. The Ideal c/a -value 1.633 is also shown by the upper line (- - -), showing that all the observed c/a -values for GaN fall well below this value.

a [Å]	c [Å]	Ref.
3.189	5.185	8
3.18	5.16	9
3.180 ± 0.004	5.166 ± 0.005	10
—	5.185 ± 0.0006	11
3.186	5.178	12
3.180 ± 0.001	5.178 ± 0.002	13
3.18 ± 0.02	5.19 ± 0.02	14
3.182 ± 0.001	5.176 ± 0.002	15
3.190 ± 0.002	5.190 ± 0.002	16
3.190 ± 0.005	5.17 ± 0.01	17
3.190	5.184	18
3.160 ± 0.008	5.125 ± 0.010	19
3.182	5.173	20
3.180	5.166	21
3.190	5.189	22
3.1683	5.1381	23
3.182 ± 0.003	5.173 ± 0.003	24
3.188	5.190	25
3.17 ± 0.02	5.16 ± 0.021	26
3.182	5.173	27
3.18	5.18	28

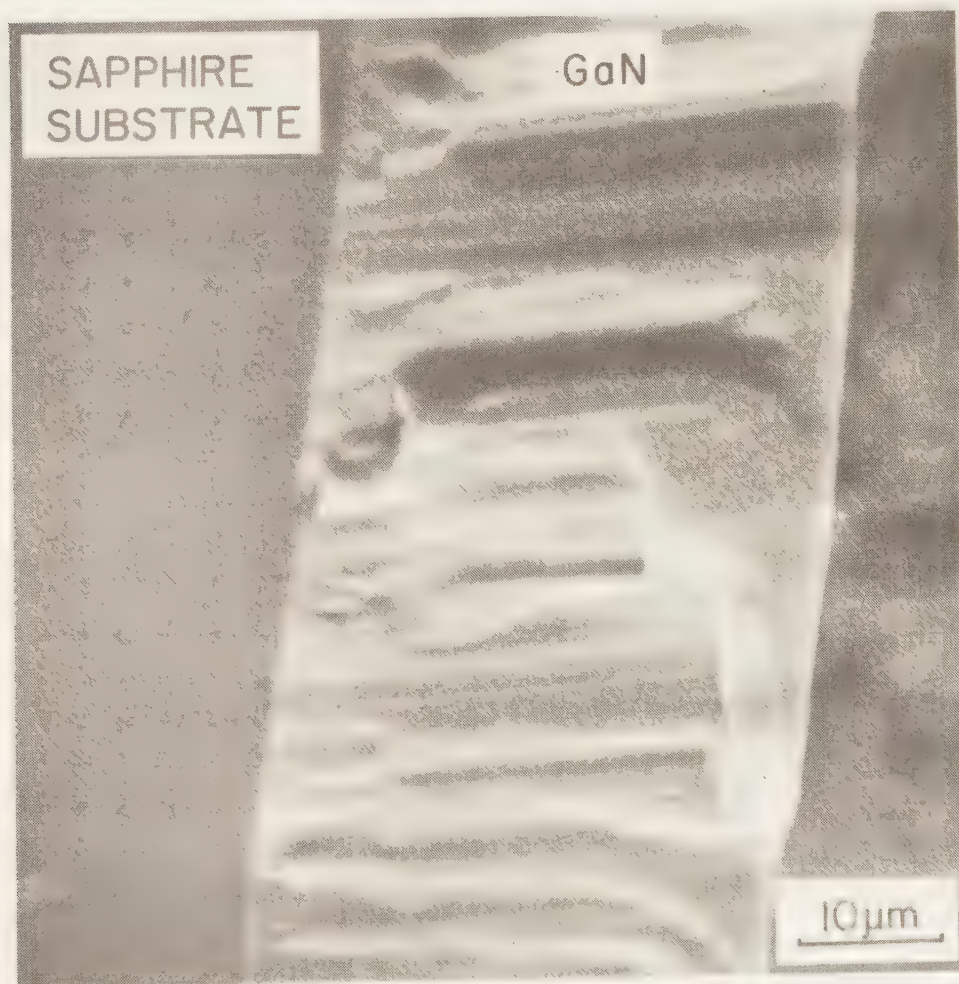
Table I. Review of lattice parameter values for GaN at room temperature from different sources in literature.

Sample	a [Å]	c [Å]	c / a
U1	3.1865 ± 0.0002	5.1822 ± 0.0003	1.6263 ± 0.0002
U2	3.1866 ± 0.0007	5.1875 ± 0.0012	1.6279 ± 0.0007
U3	3.1865 ± 0.0007	5.1869 ± 0.0012	1.6278 ± 0.0008
U4	3.1988 ± 0.0004	5.2024 ± 0.0011	1.6264 ± 0.0006
U5	3.1683 ± 0.0006	5.1483 ± 0.0021	1.6249 ± 0.0009
D1	3.1961 ± 0.0010	5.1939 ± 0.0023	1.6251 ± 0.0013
D2	3.1968 ± 0.0002	5.1972 ± 0.0005	1.6258 ± 0.0003
D3	3.1931 ± 0.0005	5.1913 ± 0.0018	1.6258 ± 0.0008
D4	3.2037 ± 0.0004	5.2106 ± 0.0007	1.6264 ± 0.0004
D5	3.1970 ± 0.0007	5.1976 ± 0.0015	1.6258 ± 0.0011
D6	3.1958 ± 0.0004	5.1925 ± 0.0010	1.6248 ± 0.0005
D7	3.1916 ± 0.0004	5.1913 ± 0.0014	1.6265 ± 0.0006
D8	3.1912 ± 0.0001	5.1902 ± 0.0005	1.6264 ± 0.0002
D9	3.1924 ± 0.0005	5.1928 ± 0.0011	1.6266 ± 0.0006
D10	3.1936 ± 0.0006	5.1965 ± 0.0011	1.6272 ± 0.0007

Table II. Measured values for lattice parameters a and c at 20 °C for different undoped (U1 - U5) and doped (D1 - D10) GaN samples grown by VPE on sapphire. The uncertainties indicated here are the standard deviations obtained in the computer evaluation of data from about 10 lines on the film.



Fig. 1a



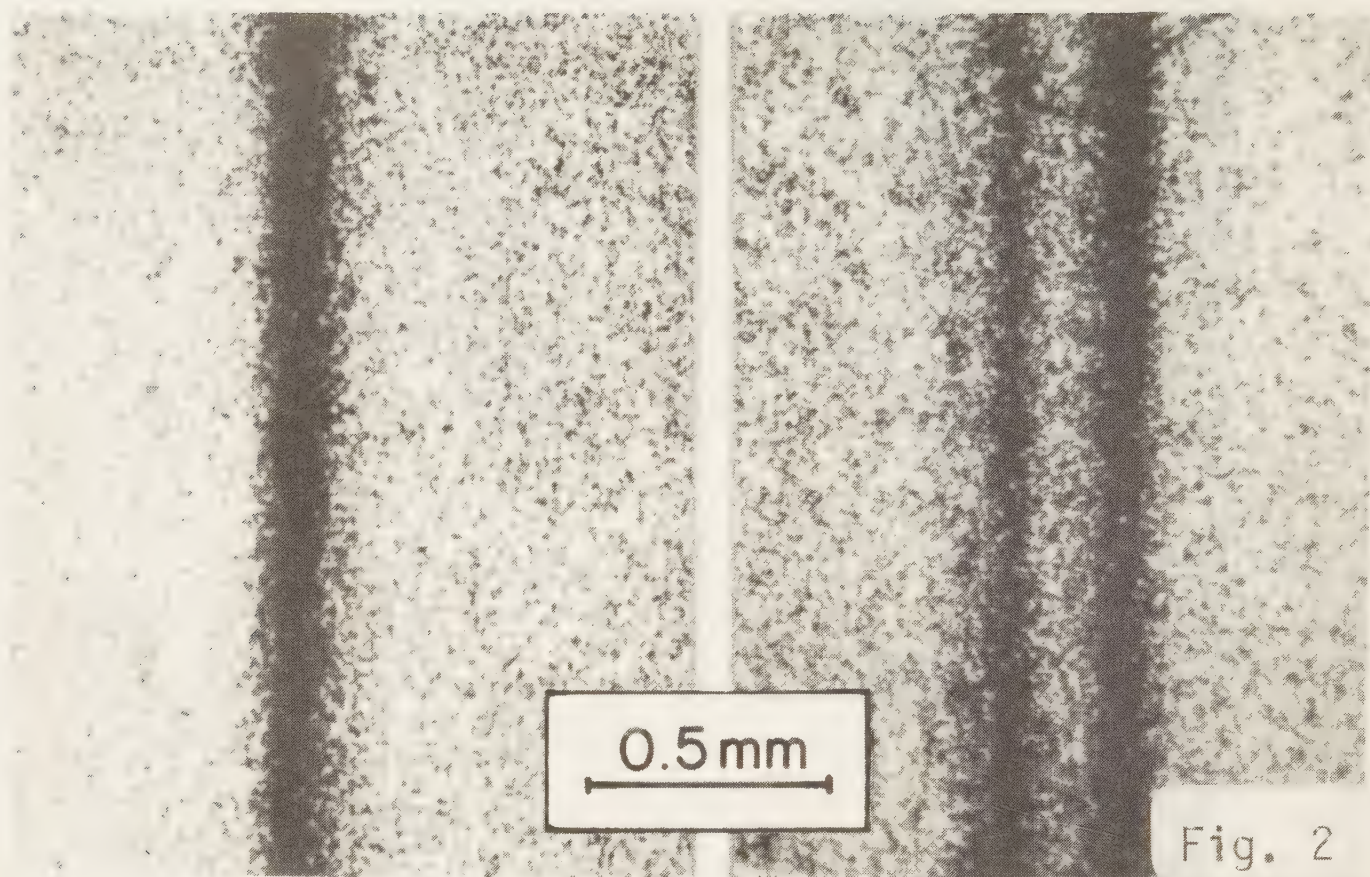


Fig. 2



Fig. 3

Properties of VPE-grown GaN doped with Al and some iron group metals

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Abstract

The influence of doping with Al and some iron group metals on optical and electrical properties of GaN epitaxially grown from the vapor phase is reported. These impurities are the main inadvertent contaminants in GaN growth, and details on the transport of these elements to the deposition area during growth are discussed. Detailed studies are performed by the SIMS-technique on impurity concentration in layers grown under different conditions of contamination.

Variations in doping over the area of the grown wafers, as well as with depth into the layer, are investigated, and shown to be significant for Al and N_2 . These investigations are complemented by SEM cathodoluminescence topographs. Photoluminescence data strongly indicate the existence of a shallow bound exciton (binding energy 12 meV) to isoelectronic Al on Ga sites in GaN. No radiative states are observed from the iron group contaminants. These (notably Fe and Cr) cause deep states efficient in electrical compensation of the material, which is easily made high-ohmic with Fe or Cr. Schottky-barrier behaviour of contacts on such material suggest the conversion to (high-ohmic) p-type conductivity.

I. Introduction

Fundamental properties of GaN are fairly well established below room temperature from earlier studies [1,2]. Preliminary data also exist for the properties of dopants incorporated into GaN [3-13] but the detailed knowledge of such defect properties (accurate binding energies, identity of defects caused by dopants) is still lacking. A major problem in the study of point defects connected with dopants in GaN is the incomplete knowledge of the role played by native defects (such as vacancies) in the incorporation of such dopant atoms. The most favourable GaN material reported so far has been grown by the VPE method on sapphire substrates [3, 14-17]. However, even not intentionally doped material usually has a free electron concentration of at least $10^{17} - 10^{19} \text{ cm}^{-3}$ at room temperature [1-3, 10, 15, 16], caused by shallow donors such as e.g. nitrogen vacancies. Previous studies of dopants in GaN have been concentrated on the IIB-elements [3-13], with the obvious aim of achieving p-type material by substitutional acceptors at Ga sites. Very little has been reported on properties of impurities such as Al or transition metals from the iron group incorporated in GaN. Since such elements have been found to easily contaminate the GaN material during VPE-growth, we have made an investigation of the influence of such dopants on the properties of GaN epitaxial layers. When such elements under certain conditions are incorporated during VPE-growth, we have found Al, Cr and Fe as the most abundant impurities, but Ni and Cu are also easily introduced inadvertently at levels well above 1 ppm. In section II below we describe briefly the crystal growth procedure, and the contamination problems that may occur during VPE growth of GaN. Results from chemical analysis of the material are presented,

and related to chemical transport processes during growth. Further, results from analysis of variations in dopant distributions over the sample area with the aid of SIMS topographs and SEM cathodoluminescence are presented. Depth distribution profiles are also presented, with particular emphasis on Al and N_2 . Photoluminescence data at low temperature for doped samples are presented in section III. These data indicate that Al causes an isoelectronic bound exciton with a binding energy of 12 meV. Properties of other acceptor-induced emissions in the material are also discussed. Section IV contains some data from measurements on electrical properties of the material, which are only preliminary, since ohmic contacts could not be established on the high resistive contaminated layers, in contrast to the case of undoped GaN. It seems like iron group elements in sufficiently high concentration make the material high-ohmic (probably p-type), and several deep centers are evident from preliminary photoconductivity data. In section V finally the collected results, in particular the luminescence data, are discussed in more detail, and some tentative conclusions are drawn on defect properties in GaN in relation to crystal growth and doping.

II. Material Preparation and Contamination Problems

II:1 VPE growth conditions

The GaN epitaxial layers used in this study were grown by a VPE-technique on sapphire similar to the one reported earlier [3]. A two zone furnace with a two inch diameter quartz liner was used,

and the NH_3 flow was introduced into the deposition zone in the opposite direction to the $\text{N}_2 + \text{HCl}$ gas flow to ensure good mixing. The purity of gases employed were $\text{HCl}:4\text{N}$, N_2 (carrier gas): $5\text{N}5$, and $\text{NH}_3:5\text{N}$, further $\text{Ga}:6\text{N}$ was always used. Since we found that (0001)-oriented substrates gave rise to smoother GaN layers with properties superior to those grown on (1 $\bar{1}$ 02)-oriented substrates, the former orientation was always used. Suitable growth rates were about 1 $\mu\text{m}/\text{min}$ at a growth temperature of 1000-1050 $^{\circ}\text{C}$. Most GaN layers investigated had a thickness of 50-100 μm . Good crystalline quality was obtained with such large thicknesses, actually the highly disordered region close to the substrate (due to the large misfit between the substrate and GaN) seems to extend at most a few μm into the GaN under normal circumstances. This does not seem to be affected by even very high doping conditions, as shown in SEM topographs of cleaved GaN wafers in Fig. 1. In Fig. 1a is shown the cathodoluminescence topograph of an undoped layer with low contamination level where the disordered area appears dark due to a drastically reduced luminescence efficiency. This region is not more than 5-6 μm thick in this case. In Fig. 1c is shown a similar picture from a layer heavily contaminated with Fe. The disordered region is also here not more than 3-4 μm in width over the cleavage area. These results indicate, that for single crystalline layers the density of extended defects such as dislocations (although probably still quite high) does not influence the optical (and probably not the electrical) properties of the material. The different properties of GaN to be reported below are therefore believed to be caused by the impurities incorporated.

II:2 Sources of contamination and transport process

It is our experience from experiments on diffusion of different elements in GaN at our growth temperatures (1000-1050°C) that diffusion coefficients for some IB, IIB or transition metal elements tried are quite low. No remarkable effects of doping from such diffusion treatment on luminescence data or electrical properties of GaN layers was observed. This seems to be in agreement with observations reported by others [18]. Therefore we conclude that doping (or contamination) of GaN with different elements is effective only during growth. The incorporation of Al into GaN in substantial amounts can occur in the presence of Al_2O_3 in the system. There are good reasons for use of Al_2O_3 instead of quartz in some minor parts of the growth system. For instance it is well-known, that Si is released from quartz boats in the presence of Ga, and can thereupon be further transported into the deposition zone [19]. (Si contamination obtained in GaN grown with a quartz crucible containing the Ga never was found not to contain more than about 10 ppm Si, however, as judged from atomic absorption spectroscopy). Another problem occurred with the holding plate for the substrates in the deposition zone. During growth this plate is covered with GaN, and a quartz plate becomes seriously degraded already after the first run by cracking during cool down, due to the lower thermal expansion coefficients of quartz compared to GaN. Al_2O_3 was found not to crack under such circumstances, and was therefore preferred to obtain good reproducibility. It was very difficult to maintain reproducibility each time the quartz plate had to be exchanged, since even a vertical difference of about 1 mm in the deposition zone seriously affected the longitudinal position for optimum growth in the zone.

The Al_2O_3 material was purified from chemical contamination by baking in HCl at a temperature substantially higher than that used in the GaN growth. Therefore the main contamination from the Al_2O_3 was the Al , which was released by decomposition of Al_2O_3 (although some residual Fe could also have been present, see below). If the residual O_2 pressure in the furnace can be kept low, as was the case in our system, the presence of Ga at $1000\text{--}1050^\circ\text{C}$ can reduce Al_2O_3 into Al -suboxides. These are volatile at this temperature and can be transported to the deposition area. We believe the vitreous Al_2O_3 is likely to be more active in this process than the single crystalline sapphire (Al_2O_3) substrate. It was also observed directly by visual inspection that after a number of runs the alumina material inside the furnace had suffered surface corrosion due to such reduction processes. A higher residual O_2 pressure in the system is expected to effectively reduce this Al transport by counteracting the Al_2O_3 reduction. We have not investigated the specific effect of high O contamination on GaN , however.

Unadvertent contamination with elements other than Al was also found to be serious under certain circumstances. As will be shown more explicitly below, transition metals from the iron group, as well as Cu , are important contaminants. With a possible exception of Fe , these can all be derived from the HCl and/or NH_3 supply. The verification of transport from the HCl -flow was done in the case of Ni and Cu by analysing the amounts of foreign metals incorporated into Ga placed in a crucible in the hot zone of the furnace under normal HCl -flow. An analytical method easily applicable to Ni and Cu contamination in Ga was developed and separately described by H Titze

[20]. The most heavily contaminated runs were those employing a halocarbon-contaminated HCl-source. In this case transported Ni was found to contaminate the Ga source at a level of 20-30 ppm, corresponding values for Cu were not more than 8 ppm. Less contamination of these elements was observed when the HCl-supply was exchanged to a halocarbon-free one, in which case contamination of the Ga with Ni and Cu could be reduced below the 2 ppm level. The rather large contamination of Ga and GaN in the presence of halocarbons in the HCl-supply is probably due to the fact that these in the presence of HCl can bind Cl. In dry atmosphere they can then attack metals, such as Cu and Ni present in the regulator materials, and form volatile compounds with these. The transport from the HCl-supply in the absence of halocarbons seems more difficult to explain, since room temperature vapor pressures of chlorides of such metals are far too low to cause any noticeable transport. It is possible that such compounds could transport as small particles suspended in the gas stream, however. As shown below Ni and Cu are present at ppm levels in GaN even in the case of halocarbon-free HCl.

Another source of contamination which has to be considered is the NH_3 -supply. It is known that dry NH_3 does attack metals, such as Cr and Fe present in regulators. The reaction products are amides with these metals, which are volatile and would transport into the furnace to contaminate growth. We believe such processes are mainly responsible for the quite large Cr contamination observed, and partly also for Fe, Ni and possibly Cu. In the case of Fe however, an additional source occurs in the presence of alumina (Al_2O_3) in the furnace. Fe_2O_3 is the most common impurity in alumina, and if

prebaking was not done for sufficiently long time, reduction of the residual Fe_2O_3 will occur in the presence of Ga during growth, whereupon contamination of GaN with Fe easily would occur. A long time prebaking of the Al_2O_3 parts at substantially higher temperature than normally used during GaN growth could eliminate this problem.

II:3 Results of impurity analysis with SIMS-technique

A number of selected GaN wafers grown under different conditions were analysed with the Secondary Ion Mass Spectrometry (SIMS) technique to obtain quantitative information on the incorporation of impurities during growth. In Table I are shown typical data for the most significant concentrations of impurities in the samples. Included is a nominally undoped sample grown with an all silica apparatus, as well as a sample rather heavily contaminated with Al, Fe or Cr due to the abovementioned circumstances. Some immediate conclusions can be drawn from the results displayed in Table I. The Al contamination is substantially less in sample 1 than in sample 2, which proves the abovementioned assumption that the alumina material used in the furnace for sample 2 is the main source of Al contamination, since for sample 1 Al can only come from the sapphire substrate. The results also show the sometimes quite large concentrations of Fe, Cr, Ni and Cu introduced by the transport processes from the supplies of HCl and NH_3 . The significantly lower concentration of Fe in sample 1 could indicate that growth in alumina-free furnace reduces Fe-contamination. Si-contamination was difficult to measure, since it interfered with N_2 (same mass number) in the investigations. We therefore made an atomic absorption spectroscopy investigation of Si

in GaN on a sample, which was intentionally doped with Si by introduction of SiH_4 into the growth zone. Si was not detected in the sample, which means it must have a concentration lower than 5-10 ppm. We conclude, that during normal runs Si is not an important contaminant in GaN, at least not on the doping levels governing the behaviour of present day material. The presence of Cl was detected in the measurements, but unfortunately a quantitative estimate could not be made. An upper limit of 100 ppm can be given, however. Naturally it is expected that some Cl will be built into the GaN material in the presence of HCl and metal chlorides transported. Unfortunately the O content could not be measured, we do not expect it to be large under our conditions of growth, however. On the other hand N_2 was detected in large amounts, which is an indication of local decomposition of GaN during growth at these temperatures (1000-1050°C), (see below).

For some of the elements it was possible to detect spatial variations in concentrations of dopants, i.e. SIMS mass micro topographs. In Fig. 2a is shown an example of such topographs for a sample heavily contaminated with Al. By comparison with the reference Ga topograph in Fig. 2b it is clear that Al is inhomogeneously distributed in the material. There is generally some continuous background of Al present, which corresponds to Al substituted into Ga sites, as evident from measurements of bandgap changes in the material (see section III below). It is possible that the bright local spots sometimes observed (not present in Fig. 2) are due to a separate phase with a high Al-content (see Fig. 3d below). The presence of such a separate phase was not detected in X-ray or optical data however.

In Fig. 3a-b are shown similar topographs for the distribution of Cu and Fe, which should be compared with the corresponding Ga topograph of the same area in Fig. 3c. Clearly Cu is distributed very inhomogeneously. A weak rather homogeneous background exist, but strong contributions are observed from defect areas, such as in this case grain boundaries between non-epitaxial crystallites (which sometimes occur under unfavourable growth conditions) and the single crystal epitaxial area. The tendency for Cu to concentrate on extended defects such as dislocations and grain boundaries is well known for a large number of solid materials, and apparently GaN is no exception in that respect. For Fe effects of some concentration to such defect areas are observed (Fig. 3b), but a pronounced homogeneous distribution is evident in this case. As a comparison is shown in Fig. 3d also the Al topograph over the same area. Evidently some local spots occur with a much higher Al-content than the average background. Further the Al-concentration is generally lower in the non-epitaxial crystallites which have grown faster in a different crystallographic direction. In the boundaries of such crystallites a high Al-concentration is always observed, however. For Cr similar clear topographs as in Figs. 2 and 3 were not obtained. It appears as Cr is partly concentrated on very local areas, but a significant homogeneous background is observed, i.e. the behaviour is similar to Fe. From Fig. 3a-d is evident, that in cases of incomplete epitaxial growth, where crystallites of a different orientation occur, very inhomogeneous impurity distributions are obtained around such crystallites. This is illustrated more drastically in a SEM topograph of a polycrystalline GaN wafer (with the crystallites oriented with the c-axis $\perp$ substrate) shown in Figs. 4b, 4c. Clear directional effects

of defect incorporation is observed; further some crystallites growing with a flat top surface are non-luminescent (Fig. 4d). The depth distribution of different impurities was also studied with the SIMS technique. (In Table I were excluded such elements which only occurred as surface contaminants (Na, K, Ca, Ti), i.e. their presence was detected only in the first micron from the surface). Most impurities showed a constant depth profile, i.e. their concentration was homogeneous along the direction of growth. There were a few exceptions to that general observation, however, the most remarkable being N_2 and Al. As shown in Fig. 5 the concentration of N_2 and Al does increase with depth, i.e. in the direction away from the GaN surface towards the substrate. In the case of GaN, grown under our conditions at a temperature above 1000°C , we believe that at defect areas inside the material decomposition of GaN can take place during growth in spite of a sufficient NH_3 pressure to counteract such decomposition of perfect material. This would explain why the region closer to the substrate, which has been present a longer time in the furnace during growth, has a higher N_2 -concentration. As noted above, the inhomogeneity of N_2 over the area of the wafer indicates that N_2 gas is present in small voids in the material, formed by local decomposition of GaN. The observation on a similarly increasing Al-concentration with depth from the GaN surface is more difficult to understand. We have found diffusion processes in GaN to be quite slow for elements from groups I and II in the periodic table, and also for transition elements. We believe Al would be no exception from this behaviour, and further we do not see how Al could be released from the single crystalline (highly stable) sapphire interface to migrate into GaN. Such a process would of course qualitatively explain a

higher Al-concentration closer to the substrate. Rather we believe some unknown peculiarity in the Al-release from the alumina and transport to the deposition zone is responsible for such behaviour.

III. Photoluminescence data

Spectral studies of photoluminescence (PL) were done with the UV-lines of a 12 W Ar^+ -laser as excitation, and with a double 0.75 m grating Jarrel Ash monochromator to obtain good resolution. A near bandgap PL-spectrum from a typical GaN-layer doped with Al and iron group metals in concentrations similar to sample 2 in Table I at 1.9K is shown in Fig. 6. The PL-spectrum of a not intentionally doped GaN layer, which was not heavily contaminated, is included for comparison. The spectrum of the doped layer starts with a high energy tail, which contains a small peak at 3.482 eV assigned to the free A-exciton. The next peak L_1 at 3.476 eV is assigned to the recombination of excitons bound to the shallow neutral donors [3]. The next peak L_2 occurs at 3.470 eV; note that no such peak is present in undoped material. The next peak L_3 at 3.461 eV is of lower intensity, and is followed by more weak emissions at lower energy, of which L_4 at 3.454 eV and L_5 at 3.445 eV are seen in Fig. 6. Due to the narrow linewidths we believe that all these emission lines are due to excitons. In addition to the appearance of a new emission line L_2 at 3.470 eV in the doped material, it is also seen from Fig. 6 that all other emissions exhibit a rigid shift compared to the spectrum from not intentionally doped material [1-3]. Since the emission spectra in Fig. 6 look the same

even if the laser intensity is lowered by a factor $10^2 - 10^3$, the shift is not dependent upon the excitation density, but merely due to change in the bandgap of the material. This increase in the GaN bandgap, which amounts to 7 meV for the rather heavily contaminated sample of Fig. 6, is most naturally attributed to the Al-content in the samples. In somewhat less Al-doped samples, a lower shift was observed. An example of a spectrum from a crystal of somewhat lower Al-concentration is shown in Fig. 7 for two different temperatures 1.9K and 40K. The spectral shift towards higher energy is here about 5 meV, further it is observed that the L_2 -line, here at 3.468 meV, is dominating the spectrum at 1.9K. At this lowest temperature, the shifted free exciton A-line is clearly observed in both Fig. 6 and Fig. 7. From the spectrum at 40K in Fig. 7 it is evident that at elevated temperatures emission is also observable from the B-exciton at about 6 meV higher energy than the A-exciton. Such enhancement of intrinsic exciton lines in emission has previously been observed for GaP crystals doped with isoelectronic substituents [21].

In the energy region 3.40 - 3.35 eV several peaks occur in the PL spectrum at low temperature (Figs. 8 and 9), most of them can be identified as LO-phonon replica of the bound excitons shown in Figs. 6 and 7. The most striking observation from Figs. 8 and 9 is that the LO-phonon replica of the L_1 -line is much weaker than the corresponding replica of lines $L_2 - L_5$. Otherwise the spectra in Figs. 8 and 9 look very similar to the corresponding ones in Figs. 6 and 7, which indicates that the coupling strengths to LO-phonons for these bound excitons $L_2 - L_5$ are similar. If one assumes that the coupling strengths to LO-phonons at very low temperature can be described by a

linear electron-phonon interaction, this leads to a Poisson distribution $I_n \sim \frac{e^{-\lambda} \cdot \lambda^n}{(n!)}$ for the different replica of each no-phonon line [22]. Previous measurements on GaN layers that were not doped, and where the L_1 -line dominated the PL-emission at low temperature, gave values of $\lambda_A = 0.04 - 0.05$ for the free exciton and $\lambda_1 = 0.001$ for the L_1 donor-related bound exciton line [2,3]. From Figs. 6 - 9 the λ -value for L_1 can only be estimated, but we can readily evaluate the values of coupling strengths for the other emissions $L_2 - L_4$. Comparing Figs. 6 and 8 we get $\lambda_1 \approx 0.001$ for L_1 , $\lambda_2 \approx 0.043$ for L_2 , $\lambda_3 \approx 0.051$ for L_3 and $\lambda_4 \approx 0.07$ for L_4 . The same evaluation on another sample (Figs. 7 and 9) give the corresponding values $\lambda_1 \approx 0.003$, $\lambda_2 \approx 0.03$, $\lambda_3 \approx 0.05$ and $\lambda_4 \approx 0.08$. It is evident that these λ -values for the coupling strength to LO-phonons in the optical transitions vary considerably between different samples. Variations in λ as large as a factor five between different samples have been observed for the L_1 exciton line. Compared to our data for undoped material it appears like a higher doping level in general tends to increase the coupling strength. It is well known that a more localized bound carrier wave function will have a higher tendency for coupling to LO-phonons. The coupling strength for the most shallow donor related L_1 -exciton is therefore expected to be smallest, in agreement with our data. The much higher values obtained for all lines $L_2 - L_5$ indicate these excitons have an origin strikingly different from the L_1 -line. This is an indication that $L_2 - L_5$ are excitons bound to different acceptor-like centers, expected to have much higher binding energies than donors. So far the shallowest acceptor binding energy observed is about 225 meV, while the typical shallow donor is only about 30 meV deep [3]. The binding energies of the excitons ($L_2 - L_5$) associated

with acceptors are obtained directly from Fig. 6 as 12 meV (L_2), 21 meV (L_3), 28 meV (L_4) and 37 meV (L_5) respectively. Measurements on a large number of samples indicate that the prominent new L_2 bound exciton line is related to the Al-contamination in the samples. It is always present in samples grown with alumina in the furnace, and was always absent when growth occurred in an all silica environment. Further we observed that the relative PL intensity ratio $L_2:L_v$ ($v > 2$) was approximately correlated with the bandgap shift towards higher energies, i.e. the intensity of the L_2 line was relatively higher for higher Al-concentration. The intensity of the donor related line was generally not correlated with any of the other exciton lines $L_2 - L_5$. Previously the L_3 line has been assigned to excitons bound to the most shallow 225 meV acceptors observed [3, 7, 8], although this has not been conclusively proved. The origin of the weaker lines $L_4 - L_5$ has to be described as still unknown; the intensity of these lines does not appear to correlate with the main contaminants besides Al, i.e. Cr and Fe, for the samples in Figs. 6 - 9. In fact we did not observe any emission definitely correlated with any of the incorporated iron group elements over the entire photon energy $1.7 < h\nu < 3.5$ eV. This is true also for very highly doped material where these metals were intentionally introduced during growth. Thus we get no direct information about the position of any Cr or Fe related impurity levels in GaN from these PL measurements.

In Fig. 10 is shown the typical behaviour of the high energy part of the DA-pair emissions at 3.25 - 3.31 eV in doped material. Detailed studies of these emissions have been reported earlier [3, 7, 8, 23, 24], and the interesting aspects taken up here are only changes

introduced by doping with Al or iron group metals. Clearly the origin of the emission observed in this range is not any of these impurities, but some unknown very commonly introduced defect in VPE GaN growth [3]. We note that the first emission peak occurs at about 3.272 eV (Fig. 10), compared to about 3.263 eV in e.g. Ref. 3. Accounting for a higher excitation intensity in the present case, causing a slight shift of the emission to higher photon energies, this shift is in excellent agreement with the observation of a 7 meV increase in bandgap observed from a study of the excitonic emission in the same crystal. The structure apparent on the high energy shoulder of this shifted DA-pair band is relevant in comparison with Figs. 6 and 8. The feature at about 3.278 eV is apparently a second phonon replica of the L_2 -line. The intensity of this replica is approximately 100 times smaller than the one-phonon replica, in agreement with the above mentioned Poission distribution typical for linear phonon-coupling. There is a second weak peak L^* at 3.294 eV, which is approximately in the correct position for a second L_0 -phonon replica of the L_1 -line (Fig. 6). Its intensity however, is about as strong as the one-phonon replica in Fig. 8, i.e. a factor about 500 too strong compared to what would be expected from linear phonon-coupling. Unless a very dramatic deviation from linear coupling occurs for the L_1 -line (excitons bound to neutral donors), we have to ascribe the 3.294 eV feature to some replica of an unresolved emission in the background of Fig. 8, close to the $L_1 - L_0$ replica observed there. The temperature quenching of this 3.294 eV line is similar to the lines in Fig. 8, which proves it is a phonon replica. Note that a very similar situation was previously observed in more pure Cd-doped samples [3]. The feature A" around 3.302 eV in Fig. 10 finally is described as a

L0-phonon replica of the line marked A' in Fig. 8. Note that A' at 3.384 eV in Fig. 8 is displaced about 2 meV towards higher energy than expected for a 91.5 meV L0-phonon replica of the A exciton (Fig. 6). Besides the intensity of the 3.302 eV line is about the same as the A'-line, which requires a strongly nonlinear phonon coupling for the assumption of a second phonon replica of the A exciton line at 3.483 eV (Fig. 6). The temperature dependence of PL emission intensities of the most prominent exciton emissions $L_1 - L_3$ was also studied, and the results are shown in Fig. 11 for $T < 43\text{K}$. At the lowest temperatures ($T < 10\text{K}$) very little variation in emission intensities are observed. In the region $10\text{K} < T < 30\text{K}$ a rather slow temperature variation is observed, with a different slope for all lines. A more drastic decrease in emission intensities was observed above 30K for all emissions. As can be seen from Fig. 11 the activation energy for quenching of luminescence in this region is 28 ± 2 meV for the bound exciton lines $L_1 - L_3$. We believe the slight difference in temperature quenching of the lines below 30K, together with the differences in coupling strength shown above, are arguments that prove the different origin of these lines, i.e. they are connected with different defects. The similarity in temperature quenching above 30K is therefore interesting, and can possibly be related to nonradiative processes involving the N-vacancy, which has a binding energy of about 30 meV [3].

IV. Electrical Properties

The influence of high doping levels of Al and iron group metals on the electrical properties of GaN was also investigated. Normally undoped GaN comes out low resistive n-type, due to a large concentration of native donors, believed to be the N-vacancies. It was found that the normally low-ohmic n-type GaN layers came out high resistive in cases of substantial incorporation of e.g. Fe or Cr during growth. A problem which seriously interfered with detailed measurements of electrical data for the Fe-doped samples was that ohmic contacts could no longer be established. Previous investigations on properties of contact materials for GaN have always been conducted on rather low-ohmic n-type GaN [6, 10, 17, 36], where all metals investigated gave ohmic contacts. This is also in agreement with our own experience with low ohmic n-GaN. For high-ohmic doped material, however, contact materials such as In, Ni and Au all gave rectifying contacts. The I-V-characteristics of such a single contact was not directly evaluated, since two similar contacts of opposite bias influenced the measurements simultaneously. Therefore a difference in current values of up to an order of magnitude can be obtained upon change of polarity, which is not surprising considering inhomogenities in the GaN layer quality over the wafer. However, for all investigated contacts on high-ohmic doped GaN the I-V-characteristics seems to be close to exponential above 0.2 V. One natural explanation of this observation of rectifying contacts is the assumption of a Schottky barrier being formed on the GaN material. This seems not to be probable as long as GaN remains n-type, since ohmic behaviour would then still be expected above a certain threshold value (1 - 2 eV), which was not observed.

Therefore we suggest that upon high doping with transition metals the Fermi level has moved down to the lower part of the bandgap to turn the material high ohmic p-type. In that case a Schottky barrier contact is expected, as observed. We can not definitely rule out that some deep Al center could also play a role in this compensation behaviour, however, since the samples highly doped with Fe and Cr were prepared under conditions of rather high Al doping. Very high resistive samples were always obtained when Fe or Cr was intentionally introduced during growth, however. It is interesting to note, that in some in-structures grown with Zn-compensation we have observed an I-V-characteristic resembling that for a schottky barrier, which indicates that also highly compensated Zn-doped GaN may indeed have p-type conduction.

Such high-ohmic Cr and Fe compensated samples show strong photoconductivity in the visible region of the spectrum. Since ohmic contacts were not obtained, we could not measure an accurate spectral dependence of photoconductivity. In Fig. 12, however, is shown an approximate such spectral behaviour measured at room temperature with constant photon flux at different photon energies. Very long time constants were involved, so the curve had to be measured point by point. Some tentative conclusions can be drawn from curves such as the one in Fig. 12. Starting at low photon energies one threshold seems to occur at about 1.9 eV, another one at about 2.6 eV. These edges are apparently related to the corresponding spectral cut off of optical cross sections related to deep level impurities, possibly Fe and/or Cr. Since the contact properties might influence even the spectral behaviour of photoconductivity, no accurate evaluation of these edges

is warranted from the present data. A third edge, probably related to shallow acceptors, is observed at about 3.2 eV. This could be related to a more shallow nonradiative acceptor introduced by these contaminants. At the bandgap a saturation of the photoconductive yield is observed, as expected for a direct gap material due to the influence of surface recombination [25].

V. Discussion

The identity and properties of point defects and simple defect complexes introduced inadvertently into semiconductors during growth, or in the cool-down process after growth, is still an area where very little detailed progress has been made, at least for the III-V-compounds. For GaN it is established that the material, if undoped, tends to become low resistive n-type, with an electron concentration far above detected levels for incorporated foreign atoms [26]. Therefore native defects have to provide the donor concentration necessary to produce such free electron concentrations, the most probable candidate for such a donor state being the nitrogen vacancy V_N . From theoretical consideration V_N is expected to be a donor in GaN, and V_{Ga} should be an acceptor [27]. A similar situation has recently been experimentally confirmed for GaAs, where V_{Ga} is an acceptor and V_{As} a donor [28]. Formation energies for antisite defects are calculated to be much higher than for single vacancies in GaN [27]. Therefore it is almost certain that the n-type conductivity of undoped GaN is due to isolated N-vacancies, which have a shallow donor binding

energy of about 30 meV [3]. The Ga-vacancies should occur in much lower concentrations, and are probably not important for the properties of presentday GaN material. Therefore foreign impurities have to be introduced as acceptors into GaN to compensate for the presence of V_N -donors. The achievement of such compensation, and a knowledge about the actual defect reactions involved, is the major step to be solved until low-ohmic p-type GaN can be made.

The low temperature photoluminescence data presented under Sec. III for material rather heavily doped with Al and some iron group metal impurities, such as Fe and Cr, give some interesting new information on the effects of Al-doping. An increase in the bandgap of GaN with Al-doping is observed, which is readily understood if Al enters Ga sites to form a dilute $Al_xGa_{1-x}N$ alloy. AlN has the same wurtzite structure as GaN, and also a very similar band structure [29, 30], i.e. a direct gap in the Γ -point, substantially higher than GaN, about 6 eV [31-33]. There has been some doubts expressed in the literature on the possibility of obtaining $Al_xGa_{1-x}N$ alloys under the growth conditions for normal GaN VPE-growth [30], but recently the preparation of such alloys over a large composition range seems to have been established [34]. Therefore a bandgap increase of about 5-7 meV as for the samples used for Figs. 6-10 would correspond to $x \approx 0.002$ in $Al_xGa_{1-x}N$, if an approximately linear variation of the bandgap with x is assumed. This compares well with the detected Al-concentration in the samples, which was about 0.18%. The highest detected concentration of Al in any GaN layer was 0.45%. Typical variations in concentration was a factor 2 over 0.2 mm. SIMS analysis was made on arbitrary spots (about 0.01 mm^2 area) on the samples,

further it should be noted that the absolute values of Al-concentration obtained from the SIMS analysis is uncertain by a factor 2.

The occurrence of a prominent new bound exciton line in GaN doped with Al is indeed an interesting observation. The bandgap shift observed seems to prove that Al predominantly occupies Ga sites. Therefore it seems natural to assume that the new exciton line is due to an exciton bound to the isoelectronic defect Al on Ga sites. This would be quite remarkable, since previously no bound states have been observed for isoelectronic substituents for group III-elements in III-V-compounds, while such bound states are very common for group V-elements [35-37]. The occurrence of a bound isoelectronic state is dependent on differences in atomic potential for the impurity and the element it replaces, but also to size differences of the atoms leading to relaxation effects upon incorporation in the lattice. There is some size difference in the case of Al in GaN, illustrated by the difference of about 2% in lattice parameters between AlN and GaN [30]. We do not want to speculate here on what would be the most important binding mechanism for an exciton at isoelectronic Al on Ga site in GaN. We note that only very weak binding occurs (12 meV), and that the binding of an exciton does not necessarily mean that any of the charge carriers can be separately bound to the center. In general one could argue, that the lower dielectric constant of GaN compared to other III-V:s such as GaP would tend to diminish the importance of screening of an isoelectronic impurity potential. This means that binding at a group III atomic site would more easily occur for GaN compared e.g. to GaP, where such binding has not been observed. An alternative possibility to an isoelectronic origin for the L_2 line would be a

complex involving Al, which could bind an exciton. The reason why we consider this possibility less likely is that we believe any complex involving more than one lattice site would be likely to exhibit a much stronger phonon cooperation, and also would not be expected to be as shallow as indicated by the L_2 line position. As mentioned above, our observation of an exciton bound to isoelectronic Al on Ga sites in GaN would be the first observation of such binding on group III sites in III-V-semiconductors. We have undertaken preliminary attempts to incorporate group V isoelectronic impurities in GaN. No definite indications of bound states have to date been obtained. The most obvious candidate for a bound state would be Bi on N sites, but no luminescent state was observed upon introduction of Bi during growth. It is possible that the amounts of Bi incorporated on N sites in GaN was much reduced by a limited solubility, however. P and As were introduced in GaN by ion-implantation [11], but no characteristic spectra were found. Recently, such spectra have been reported by other workers [38], however, indicating the presence of specific defects associated with As and P in GaN. Whether these would be the simple isoelectronic substitutional centers remains to be proved.

The other exciton lines L_3 - L_5 observed and discussed above indicate the presence of more acceptorlike centers binding excitons. It is noteworthy, that we do not observe any corresponding DA-pair emissions for each of these lines, as would otherwise normally be expected. The 3.26 eV DA-pair emission commonly observed is due to an unidentified shallow acceptor, which in pure samples shows some correlation in intensity to the L_3 bound exciton line [1, 3]. Our chemical analysis of the material, partly displayed in this paper, does not shed any

light on the origin of this shallow acceptor with a binding energy of about 0.225 eV [3]. A possible reason for the absence of other DA-pair emissions could be that most acceptors are considerably deeper than the 0.225 eV one. So it has been shown, that the most shallow Zn-induced acceptor has a binding energy $E_a = 0.37 \pm 0.04$ eV [39]. Mg also appears to have a reasonably shallow acceptorlike state [8, 9, 40], with an estimated binding energy of about 0.3 eV. These impurities were not studied in the present work. It would seem that most other group IIB acceptors are deeper [3, 11, 41], and give rise to broad emission bands well below the energy bandgap. This is probably the case also for the common contamination impurities from the iron group studied in this work. It is a general observation, that it is more difficult to obtain efficient radiative recombination from deep states, due to their tendency to favor nonradiative recombination processes [42]. This would explain why iron group impurity related luminescence from deep acceptorlike states is not observed, although the existence of such states was demonstrated by electrical data. (Sec. IV. above). Any conclusions on the possible binding energies of the acceptors responsible for $L_3 - L_5$ can probably not be drawn from simple arguments based on the so called "Haynes rule" $E_{ax} \approx 0.1E_a$ [43], which seems to work excellent for Si. Recent work on other more polar materials, notable ZnTe, shows that no such relation between the binding energy of acceptors E_a and the corresponding binding energy of excitons to such neutral acceptors E_{ax} holds [44].

VI. Conclusions

A study of the influence of doping, in particular with Al and impurities from the iron group, on some properties of GaN VPE-grown epitaxial layers is reported. It has been found that such metals can be easily incorporated inadvertently into the material during growth, due to contaminants in the HCl supply. We have studied the possible mechanisms for such contamination during VPE-growth, by analysing contamination in Ga as well as GaN for various growth conditions. The inadvertently introduced impurity concentrations in GaN grown by VPE was analysed with the SIMS technique. Topographic studies show that in single crystalline material large area variations in doping concentration occurs, especially for Al. In polycrystalline material a large enhancement of doping was observed close to grain boundaries for most impurities. Depth profiles of impurities are constant with the exception of Al and N_2 , where significantly larger concentrations were obtained close to the substrate. For N_2 our results indicate that a lower growth temperature than the one employed in our work (1025 - 1050°C) could be advantageous. Luminescence data show an increase in bandgap of as much as 7 meV correlated with Al doping. A new shallow bound exciton line with a binding energy of 12 meV is discovered, and seems to be connected with Al. A marked enhancement of intrinsic emissions indicate that a state with properties similar to previously studied isoelectronic states in III-V-compounds has been introduced, which supports the idea that an exciton is weakly bound by Al occupying Ga sites. Several other bound exciton lines of higher binding energies could be related to different unidentified acceptor-states from studies of their respective coupling strengths with optical phonons in PL

spectra. No clear evidence for radiative centers related to iron group metal impurities was found in the region $1.7 \text{ eV} < h\nu < 3.5 \text{ eV}$.

The incorporation of Cr and Fe as efficient compensating acceptors has been studied in preliminary electrical measurements. It was found that high-ohmic material was obtained, but ohmic contacts could not be established. A Schottky-barrier type behaviour might indicate that the material had turned p-type, and photoconductivity data show at least 2 thresholds for optical cross sections introduced by the doping of these iron group metals.

VI. Acknowledgements

We are deeply indebted to H Titze and A Lodding for a fruitful cooperation in chemical analyses. We are very grateful to L Å Ledebo for assistance in acquiring SEM-data. We also thank the Swedish Board for Technical Development for financial support.

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Figure Captions

Fig. 1 SEM cathodoluminescence topograph of a cleaved edge of an undoped GaN layer (1a), compared to the corresponding SEM surface picture (1b). Similar pictures are shown for a GaN layer heavily doped with Fe (Fig. 1c: cathodoluminescence, Fig. 1d: surface picture). Within a few μm of the substrate the GaN material has a high defect density, and therefore shows very low luminescence intensity. For the Fe-doped layer, Fe was introduced after the first about 10 μm of growth. Clearly Fe causes a considerable reduction in CL efficiency, as shown by the increasing darkening after the first 10 μm of growth in (1c).

Fig. 2 Massmicrographs of Al (2a) compared to Ga (2b) of an area about 250 μm in diameter of an Al-contaminated GaN layer, obtained by the SIMS technique. Bright contrast in Fig. 2a is a direct measure of the Al concentration, in areas where the Ga signal (2b) shows a uniform brightness. Thus large area variations in Al-doping is manifested in this sample. The dark hexagons are nonepitaxial GaN crystallites, and should be disregarded in the comparison between 2a and 2b.

Fig. 3 SIMS massmicrographs of Cu (3a), Fe (3b) and Al (3d), compared to the Ga signal (3c), for an area of a GaN wafer contaminated with both Al and iron group metals (similar to sample 2 reported in Table I).

Fig. 4 SEM cathodoluminescence topograph over an area of a polycrystalline epitaxial Zn-doped GaN wafer (4b), compared to the SEM surface picture (4a). As shown in the enlarged portions in 4d (CL) and 4c (surface picture), crystallites grown with a flat top section, appear nonluminescent. Also note the regular directional variations in CL intensity within each crystallite in Fig. 4b and 4d.

Fig. 5 Depth variations of concentration of Al (a) and N_2 (b) for a 46 μm thick Al contaminated GaN epitaxial layer, obtained with SIMS technique. Note that the concentrations increase significantly with depth from the top surface in both cases.

Fig. 6 Near bandgap part of the 1.9K photoluminescence spectrum for two epitaxial GaN layers, nominally undoped (---) and heavily contaminated with Al (—), measured with above bandgap excitation (3511 Å + 3514 Å). The spectrum for the undoped layer has been shifted 7 meV towards higher photon energies, to compensate for the shift in bandgap towards higher energy with Al-doping.

Fig. 7 Photoluminescence spectra near the bandgap for an Al-doped epitaxial GaN layer measured with above bandgap excitation (3511 Å + 3514 Å). Spectra are shown for two different temperatures, 1.9K (—) and 40K (---). The spectra are normalized by multiplication of the 40K curve by a factor 24.

Fig. 8 Lower energy part of the emission spectrum of the same heavily Al contaminated crystal as in Fig. 6 at 1.9K showing LO-phonon replica of excitonic emissions. The intensity is multiplied a factor 50 compared to Fig. 6.

Fig. 9 Lower energy part of emission spectra for the same sample as in Fig. 7 at 1.9K (—) and 40K (---) respectively, showing LO-phonon replica of excitonic emissions. Amplitudes are increased by a factor 20 (for both curves) compared to the data shown in Fig. 7.

Fig. 10 Part of DA-pair emission peaking close to 3.272 eV in the same crystal as in Figs. 6 and 8 at 1.9K. The small peaks on the high energy wing are phonon replica of peaks in Figs. 6 and 8. The intensity is multiplied by a factor 50 compared to Fig. 6.

Fig. 11 Temperature dependence of emission intensities for the excitonic lines L_1 ($\nabla \nabla \nabla$), L_2 ($\times \times \times$), and L_3 ($\bullet \bullet \bullet$) below 43K.

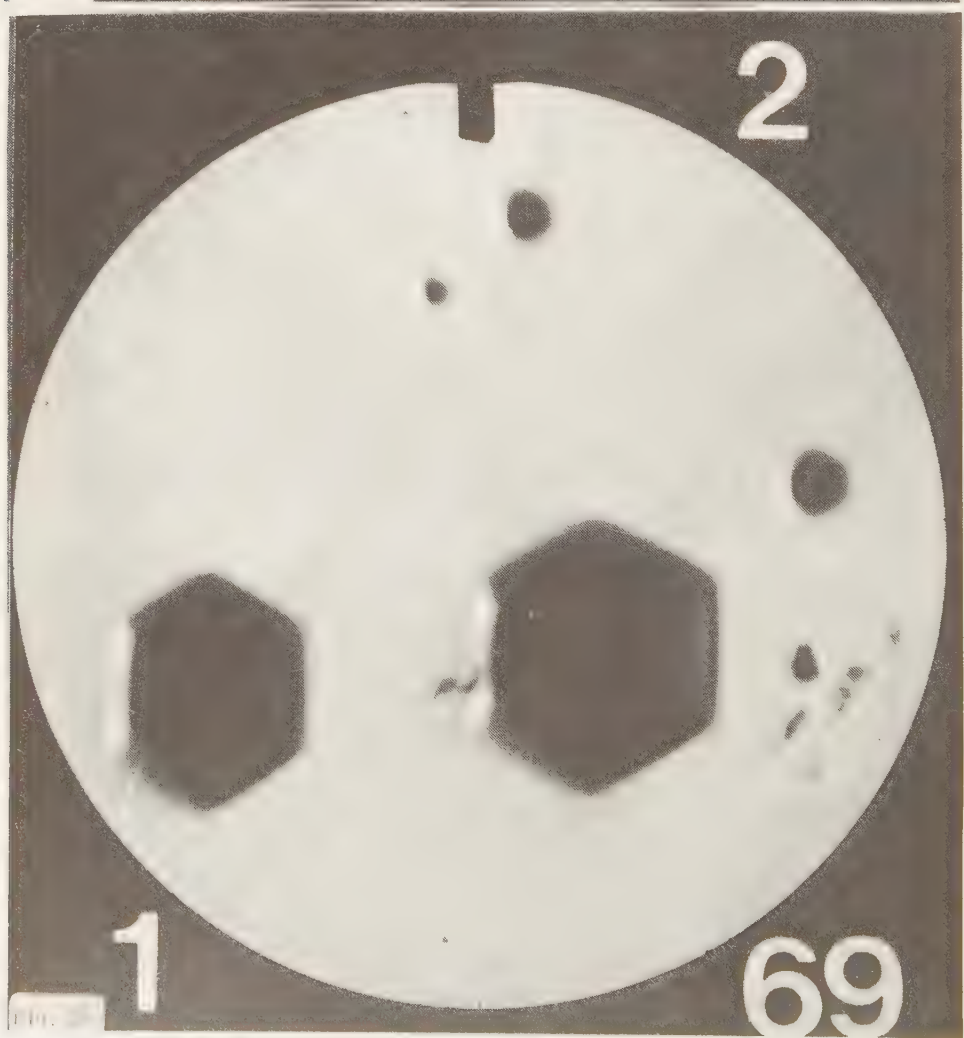
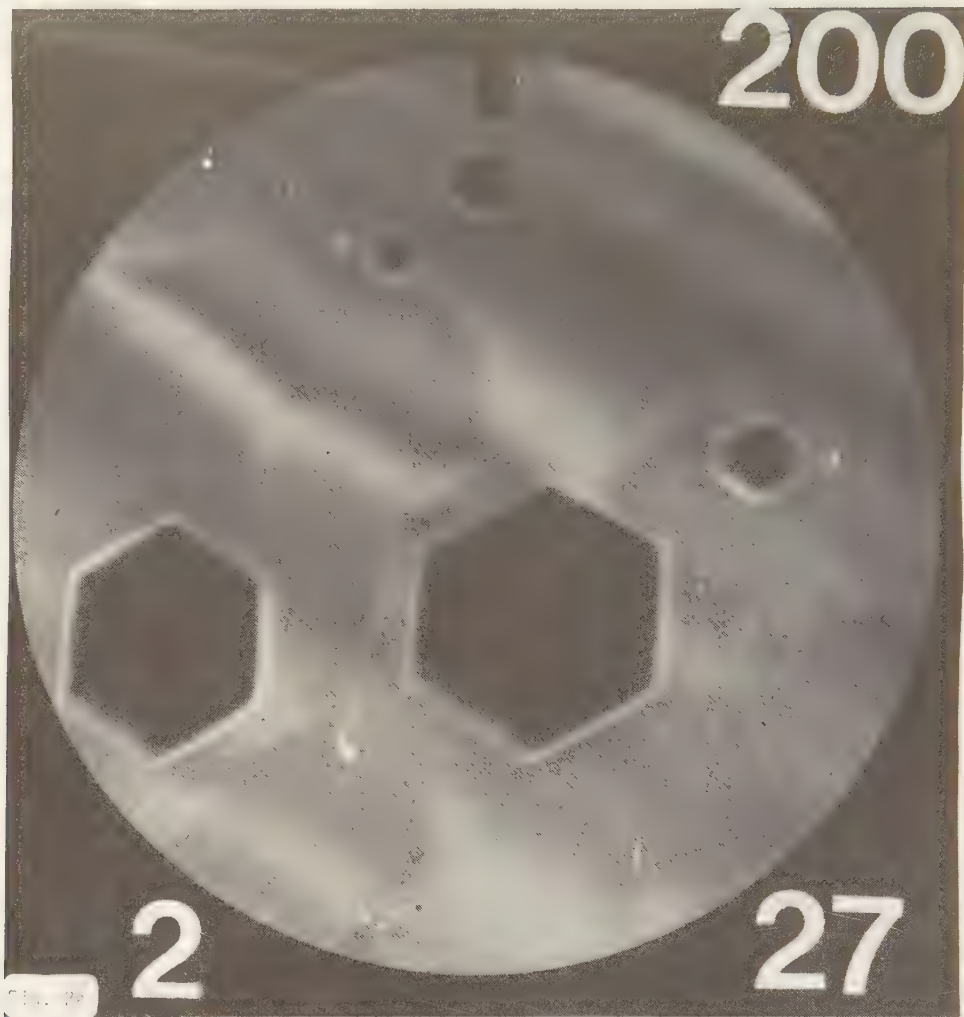
Fig. 12 Photoconductive yield at room temperature for a high-ohmic GaN crystal compensated with Fe and(or) Cr at the 75 ppm total level. Approximate thresholds for optical cross sections are indicated.

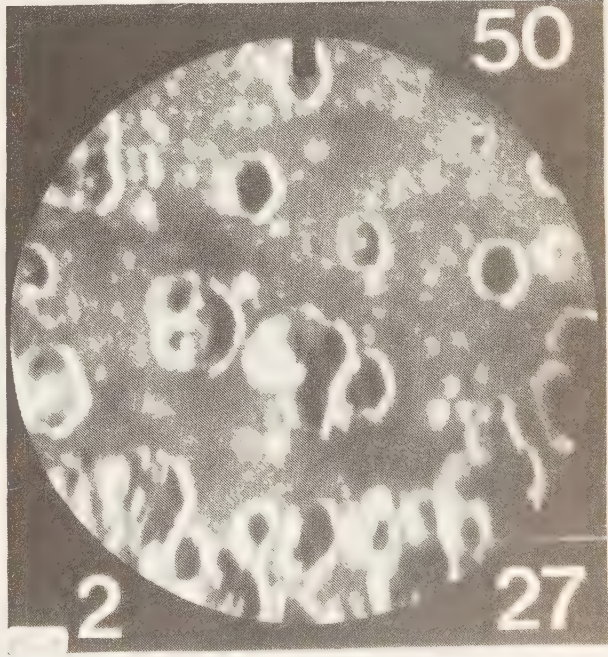
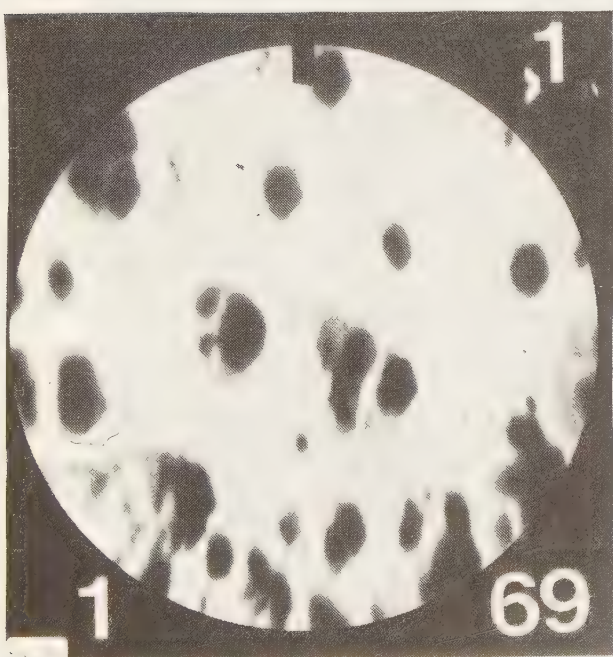
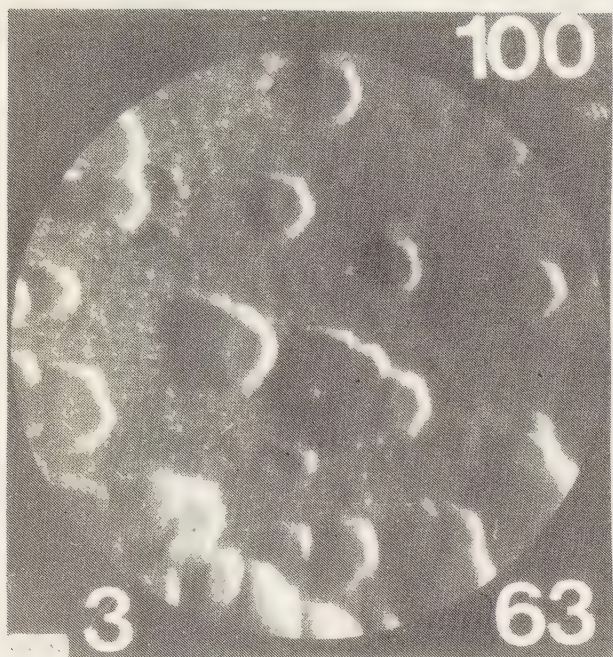
Element	Concentrations	
	Sample 1	Sample 2
Al	30	1710
Cr	< 5	15
Fe	< 20	60
Ni	24	21
Cu	4	6
Si	< 10	< 10
Cl	< 100	< 100

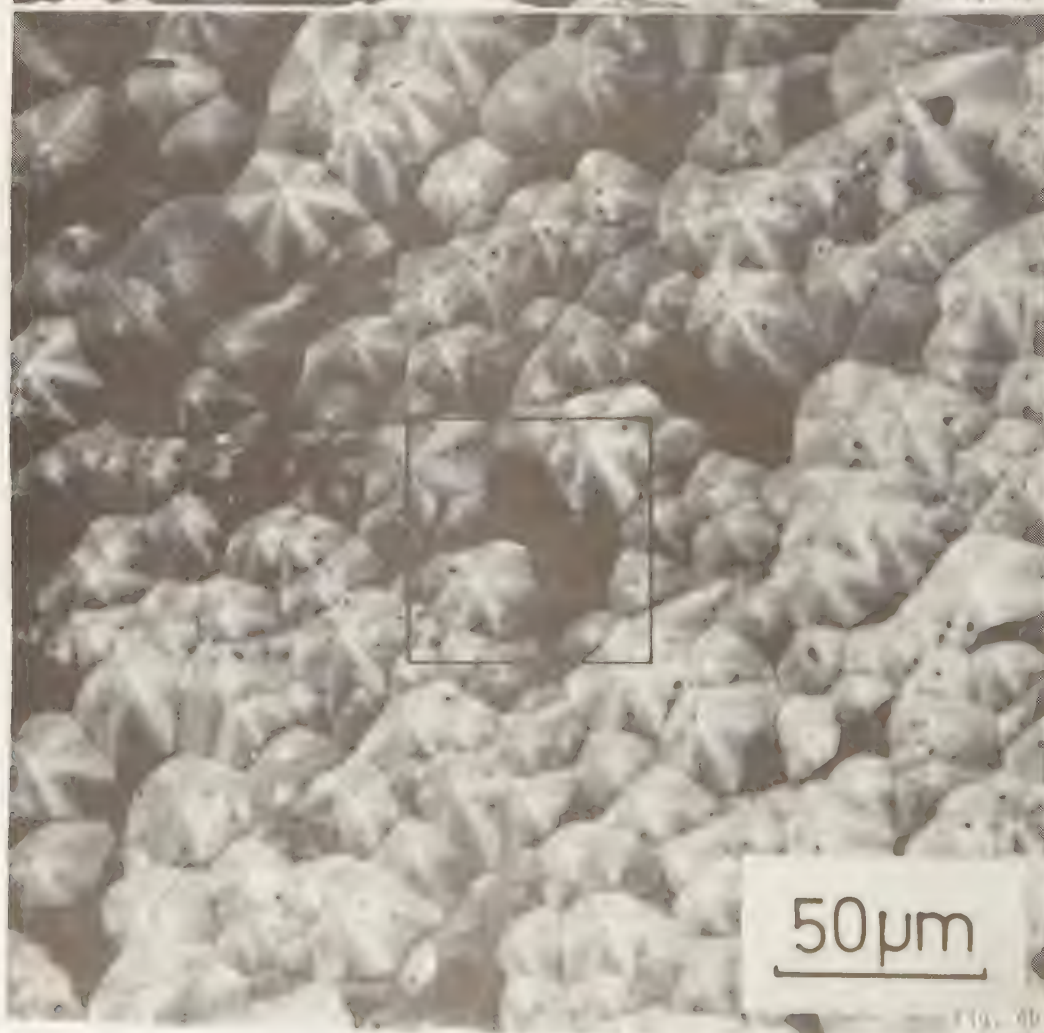
Table I. Concentrations of impurity elements (in atomic ppm) for 2 samples of GaN. Sample 1 is a typical sample grown in an all silica apparatus using halocarbon-free HCl. Sample 2 is grown with alumina parts in the furnace system and halocarboncontaminated HCl-source.

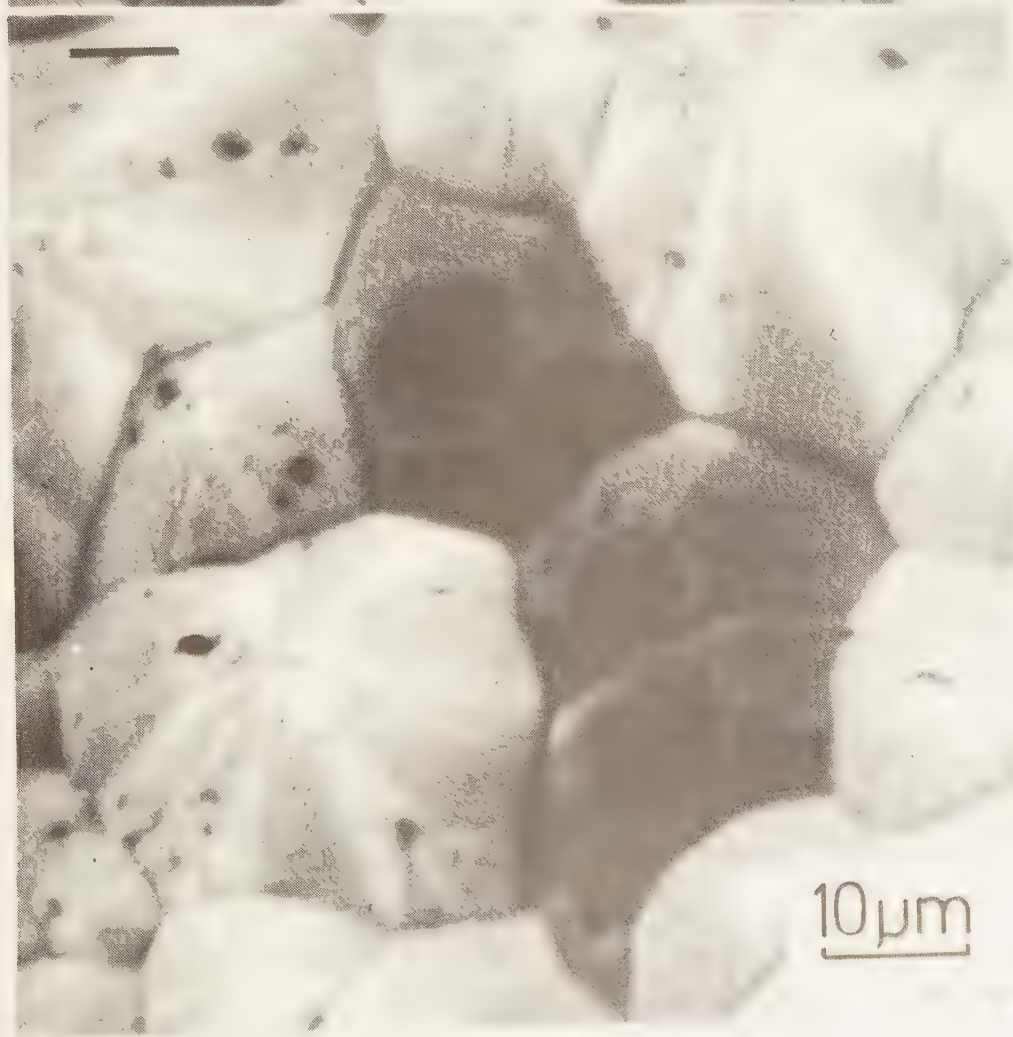












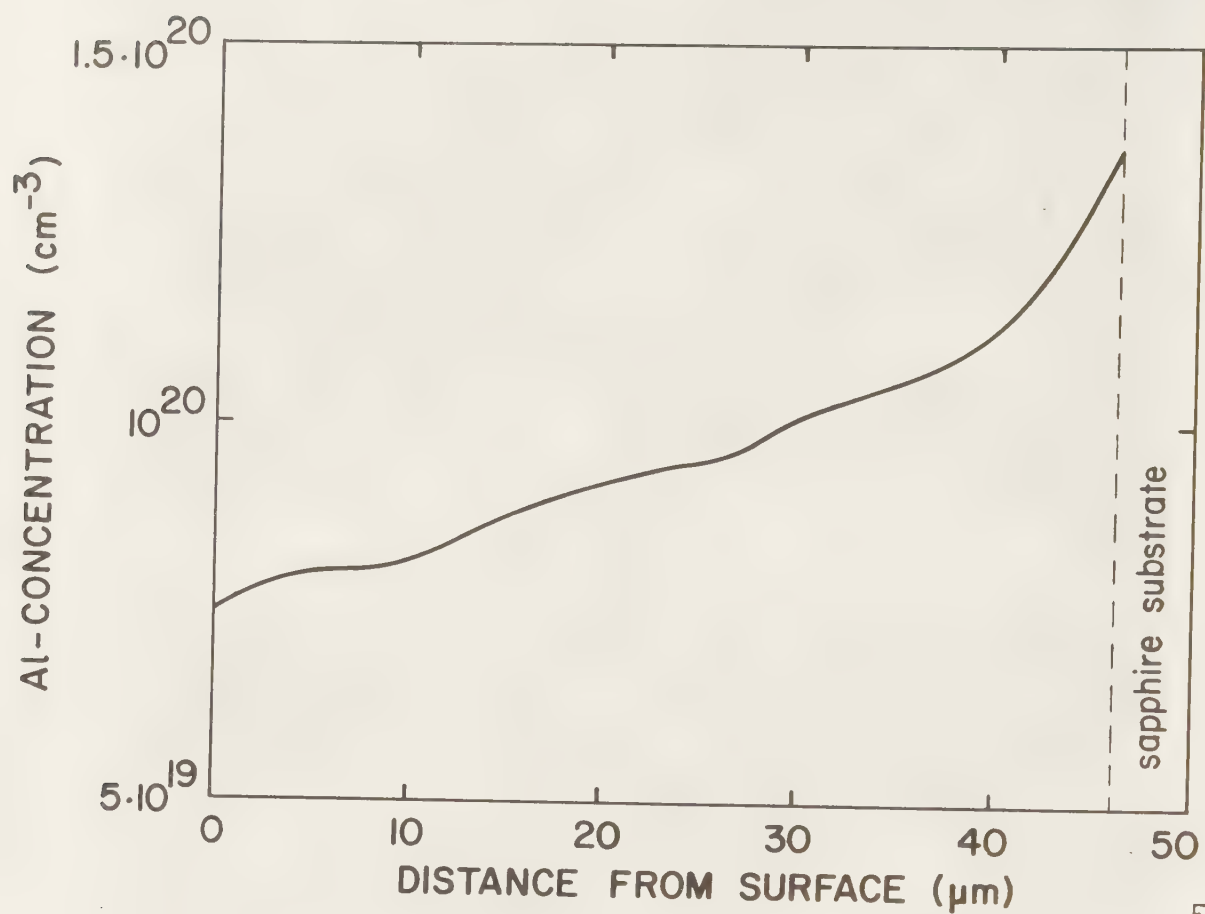


Fig. 5a

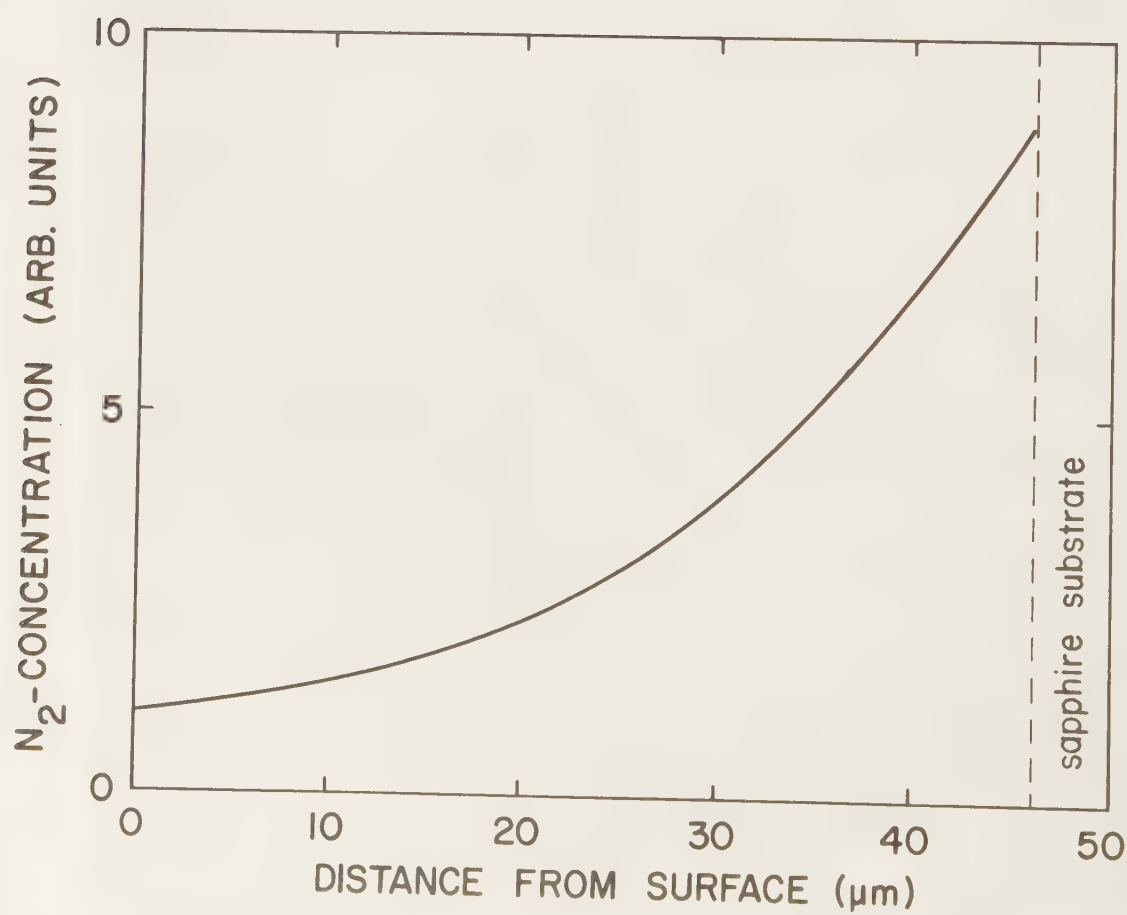


Fig. 5b

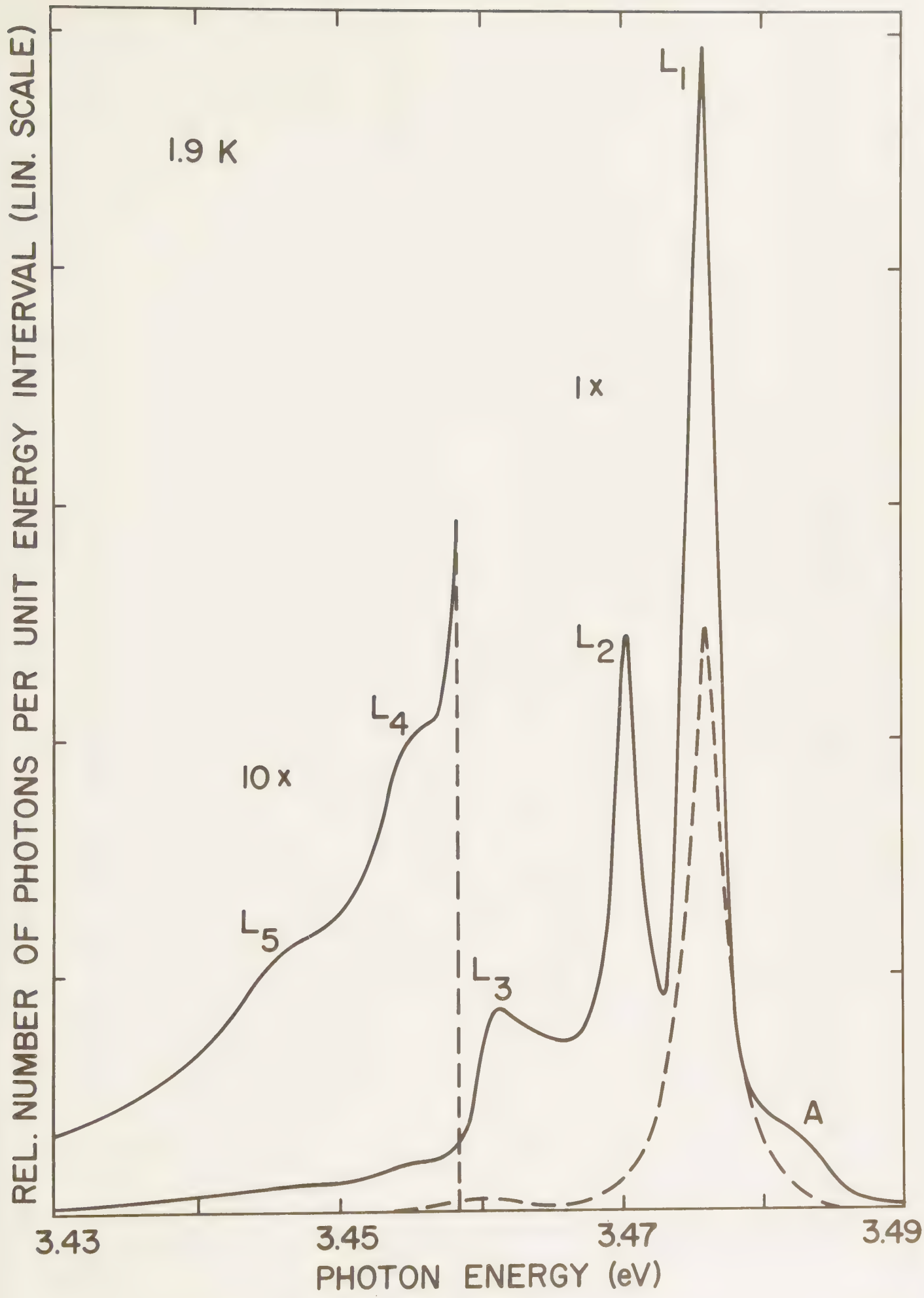


Fig. 6

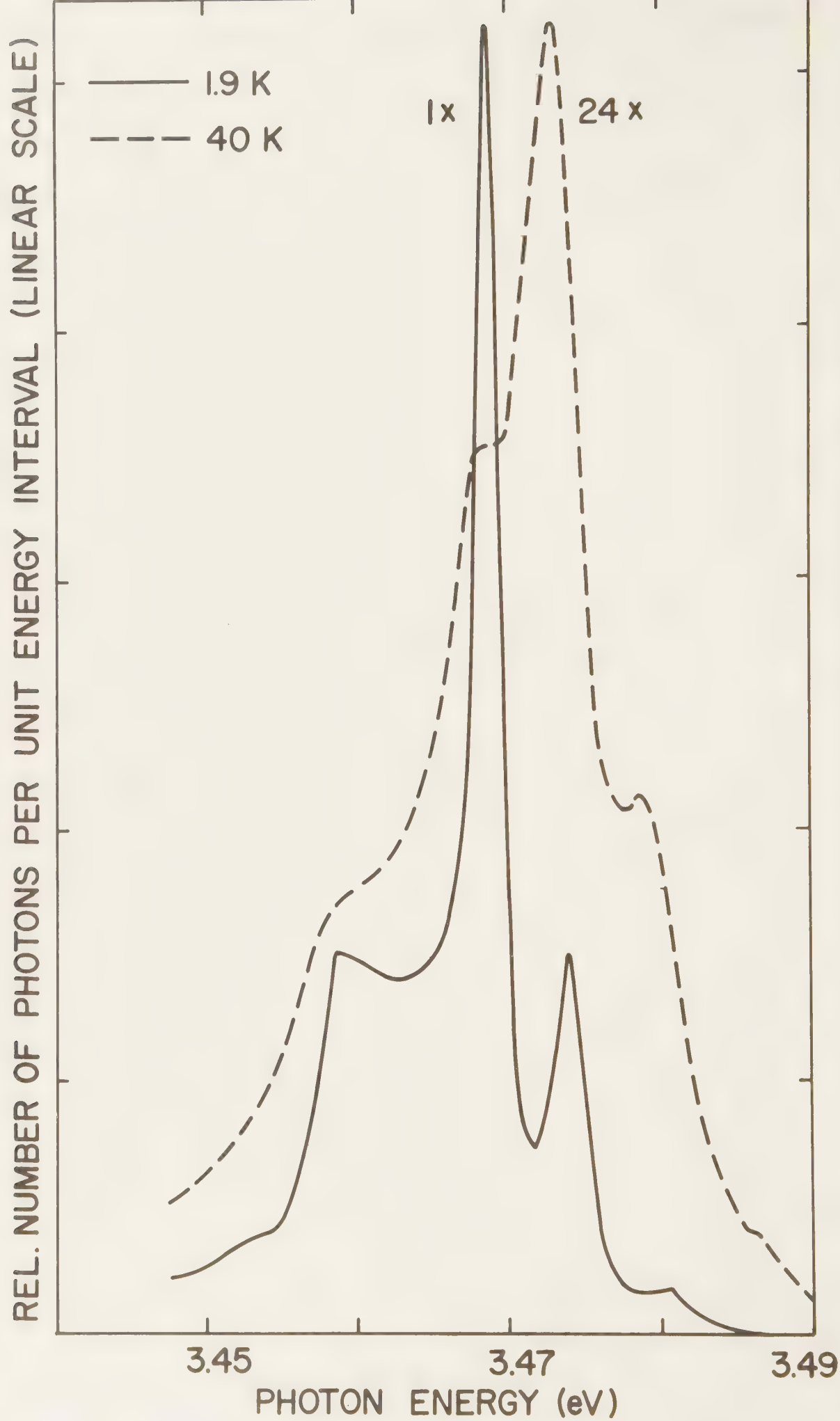


Fig. 7

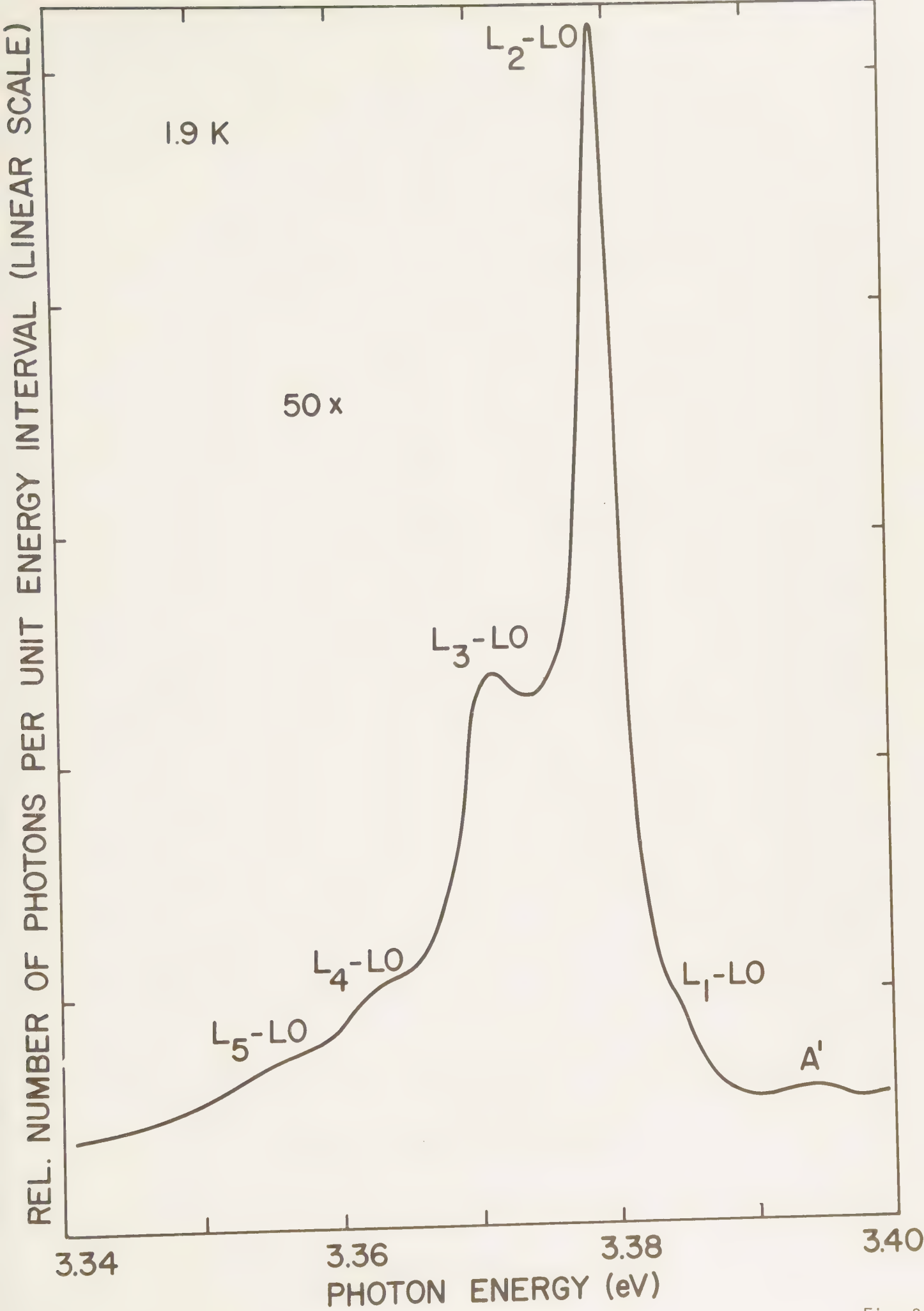


Fig. 8

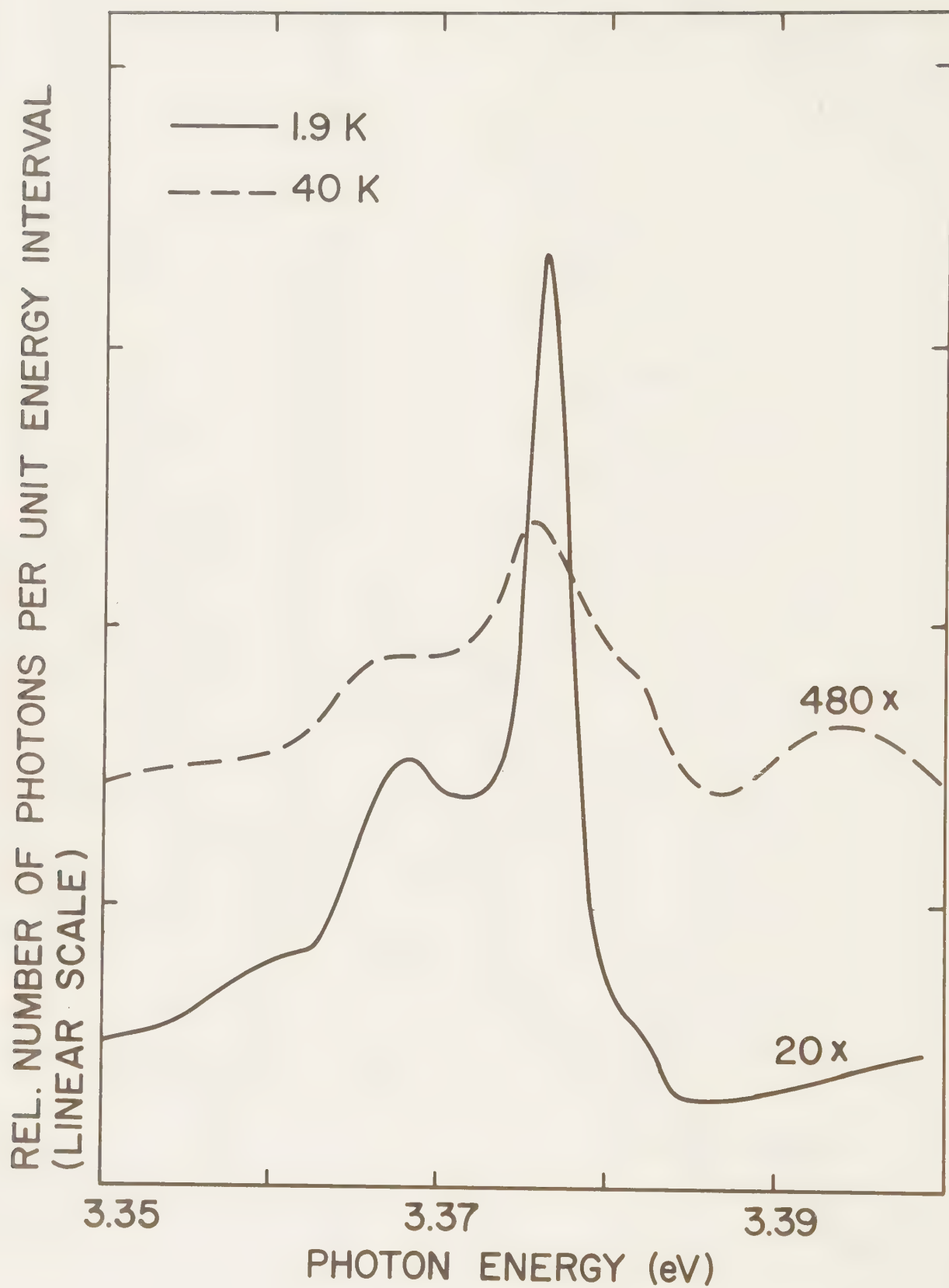


Fig. 9

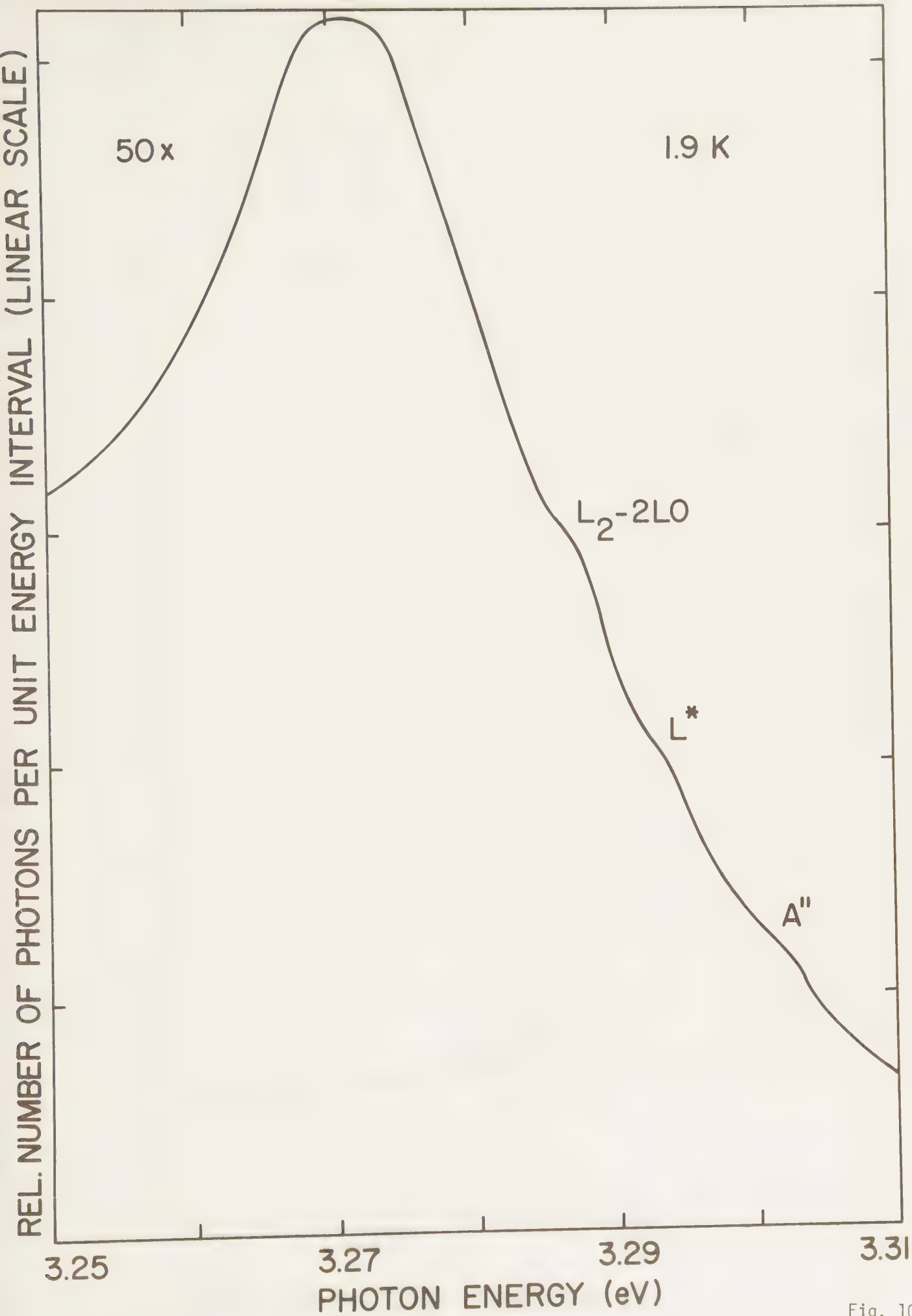


Fig. 10

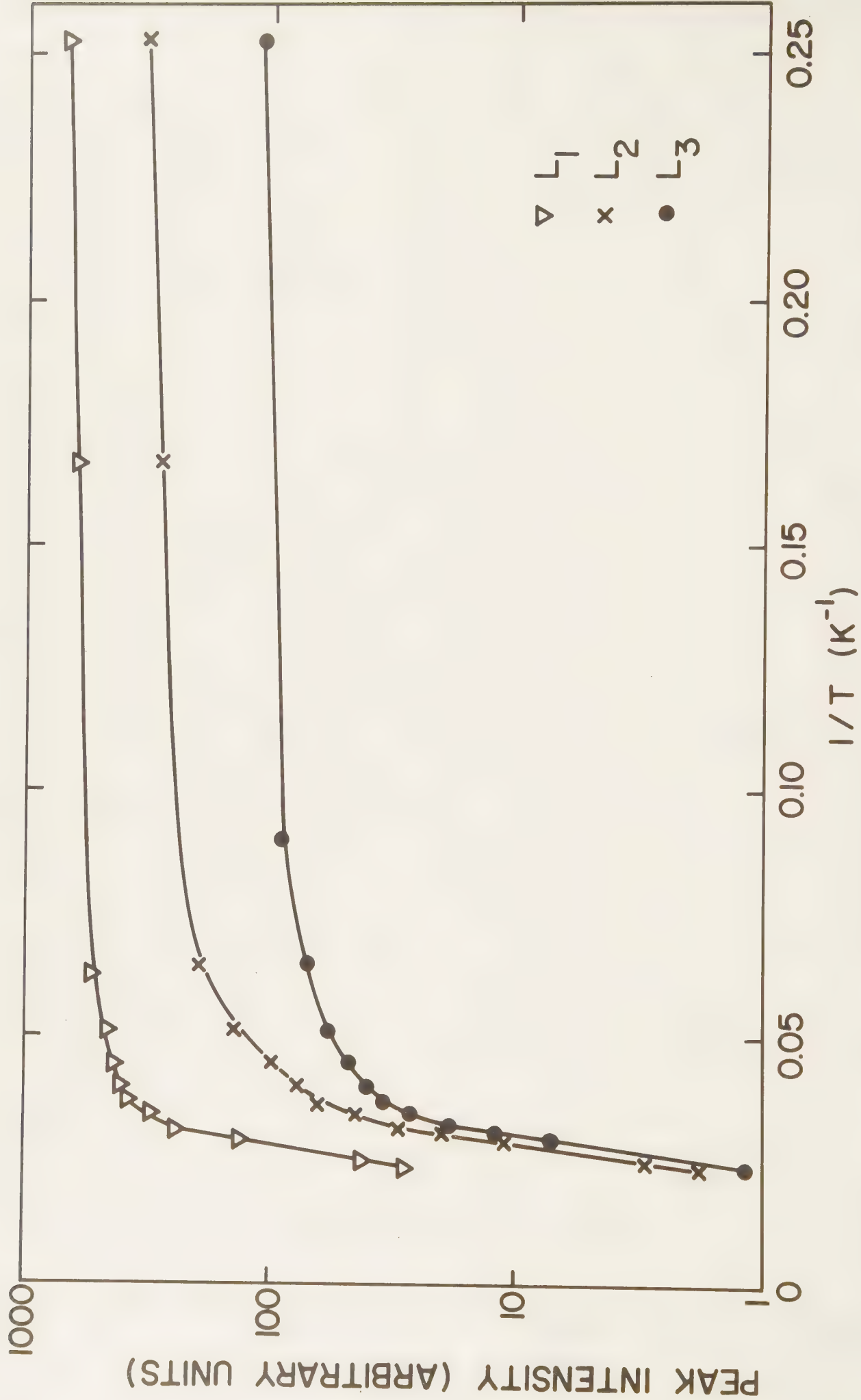


Fig. 11

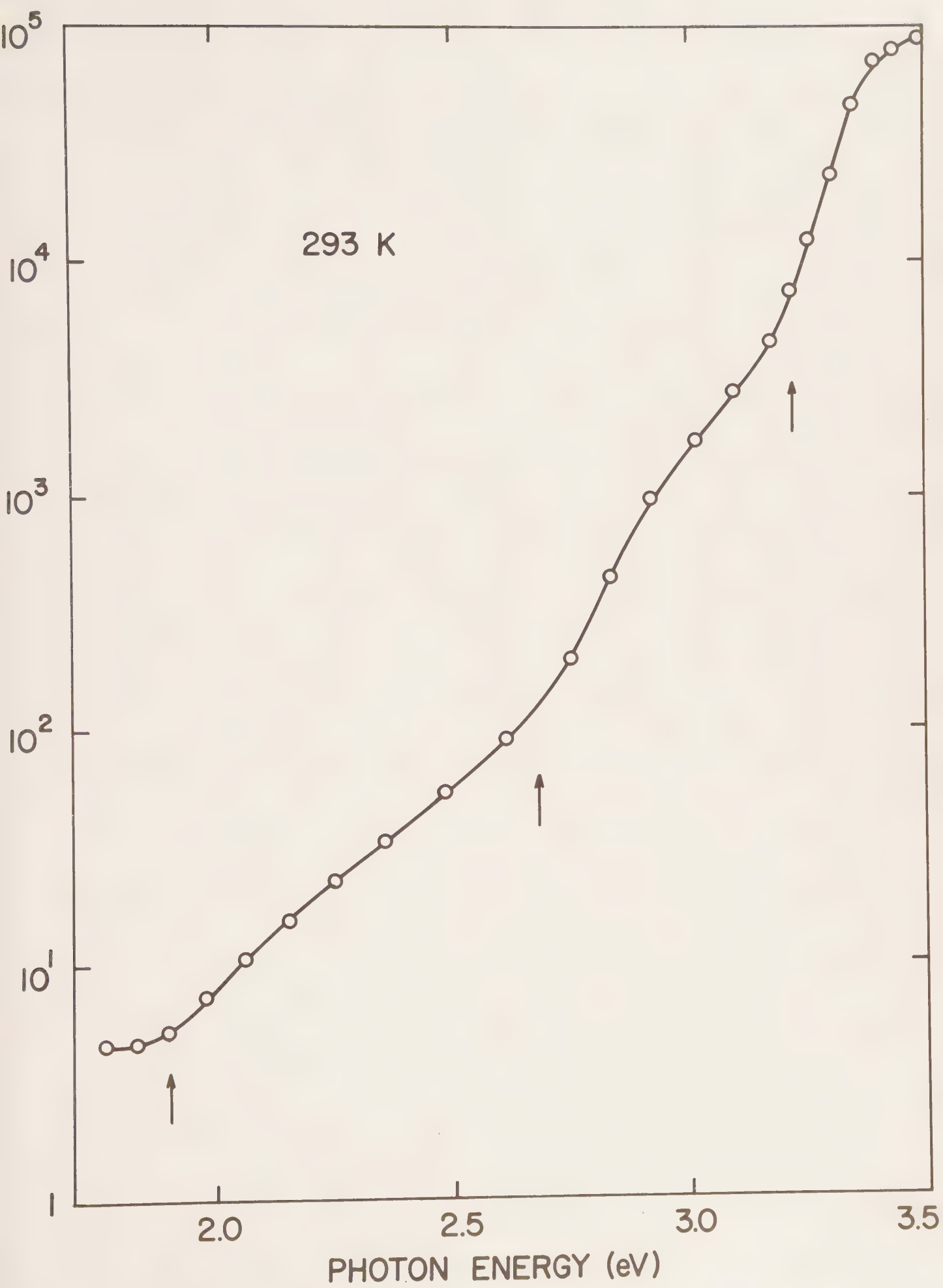


Fig. 12

Properties of Zn-doped VPE-grown GaN:

I. Luminescence data in relation to doping conditions.

by

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Abstract

Experimental results on optical and electrical properties of VPE-grown GaN doped with Zn under various conditions of growth are presented. The incorporation of Zn into GaN was found to be critically dependent on growth conditions. Four different Zn-related acceptorlike centers A - D were found to occur, with broad radiative emissions peaking at 2.87 eV (A), 2.6 eV (B), 2.2 eV (C) and 1.8 eV (D). Their broad shape was found to be due to a moderate lattice relaxation upon optical transitions. A linear model for phonon coupling was found adequate, with a principal mode resonant with the optical band ($\hbar\omega$, varying between 74 meV (A-level) to about 84 meV (C-level)) and an additional lower energy mode, yielding Franck-Condon shifts for these centers $\Delta_{FC,A} = 0.25 \pm 0.03$ eV, $\Delta_{FC,B} = 0.25 \pm 0.04$ eV, $\Delta_{FC,C} = 0.28 \pm 0.04$ eV and $\Delta_{FC,D} = 0.28 \pm 0.05$ eV. Data for electrical compensation related to the occurrence of these different emissions indicate that the A-level could be the Zn_{Ga} substitutional acceptor, while the more efficiently compensating B - D-levels might be associated with Zn occupying N sites.

1. Introduction

Investigations on the III-V-semiconductor GaN have been intensified during the last decade, mainly due to the potential interest of this high bandgap material ($E_g \approx 3.5$ eV) for light-emitting devices. Most of the effort is still concentrated on the exploration on suitable growth conditions. The obvious aim is to be able to prepare GaN single crystalline material with a controlled doping of shallow donors and acceptors. This problem is still not solved, and the shallow centers are far from unambiguously explored, as far as chemical identity and binding energies are concerned [1, 2]. Further, low-ohmic p-type conduction could so far not be reproducibly realized. More detailed investigations are necessary to establish the influence of defects (such as doping atoms) on the electrical and optical properties of the material. Since the preparation conditions for GaN are complicated by its severe thermal instability above about 1000°C [3, 4, 5], the thermal history of a sample does influence its properties to a large extent, in addition to the influence of doping. Therefore, any investigation of impurity-related properties of GaN should be closely related to the growth conditions of the material.

From earlier work it has been established that Zn is an interesting acceptor dopant, since it is capable of compensating the intrinsic donors (presumably N vacancies) in GaN to generate high-ohmic material [6-12]. Light-emitting devices based on such Zn-doped material have also been prepared on a laboratory scale [13-19], sometimes with radiative efficiencies which are quite attractive [13]. The detailed mechanisms involved in the radiative emission from Zn-doped material have not been established, however, in spite of some rather detailed investigations [2, 8, 20]. Most previous

studies were concentrated on the blue 2.87 eV emission, which is always introduced with Zn-doping. This emission is rather broad (halfwidth about 0.35 eV) due to moderately strong phonon interaction in the radiative transitions. Therefore, features of the purely electronic transitions at the high energy edge could not previously be studied, and consequently previous estimates for the position of this Zn-related level are rather scattered, the distance from the valence band being estimated to 0.3 - 0.7 eV [2, 6, 18, 20, 21]. We have found that in some crystals phonon structure can be observed on this blue emission band, and thus an investigation of the properties of the electronic transition is possible from our data, by a deconvolution procedure [22]. Also details in the phonon interaction in the radiative transition (due to lattice relaxation upon change of charge state of the defect) could be evaluated. Our analysis shows that strong broadening effects are present even in the lineshape for the electronic transition.

Unlike most previously reported work on Zn-doped GaN we find that Zn introduces several deep states in GaN, and further that the occurrence of these different states depends critically on Zn doping and other preparation conditions. Several different Zn-related centers have also recently been reported by another group [8]. At low Zn-doping only the blue 2.87 eV emission is observed, but at high doping levels ($> 10^{19} \text{ cm}^{-3}$) additional broad emission bands are observed peaking at about 2.6 eV, 2.2 eV, and 1.8 eV. We report a detailed spectral study of these emissions as well, yielding the approximate discrete level positions and phonon coupling parameters in the optical transitions.

A detailed evaluation has been done of the temperature dependence of emission properties. The shift of the emission with temperature is related to the corresponding shift of the deep level in the bandgap. The observed temperature broadening of the high energy edge of the emissions is also studied, and was found to be larger than expected from a convolution of the evaluated electronic emissions with phonon coupling parameters determined by the abovementioned analysis of emission shape at the very lowest temperature. These temperature dependent properties are related to observations on optical cross sections for these same Zn-related centers, to be reported separately [23].

In Sec. II below the conditions of crystal growth and Zn-doping are described. Further electrical data for the samples studied, as well as an evaluation of Zn concentration and distribution by secondary ion mass spectrometry (SIMS), will be presented.

The experimental results on photoluminescence (PL) spectra are described under Sec. III. The analysis of phonon coupling in a linear configuration coordinate (CC) model is also included, as well as the influence of temperature on emission properties.

In Sec. IV the luminescence data are discussed in more detail, in relation to growth conditions. Details in the doping conditions are discussed and results of doping is compared with previously reported behaviour. A specific model is suggested for the identity of the four Zn-related centers, in relation to results on luminescence and electrical data. Possible mechanisms for the electronic

broadening behaviour of optical spectra at high doping levels are also discussed, as well as the details in phonon broadening.

In Sec. V the most important conclusions from this work are collected.

II. Sample preparation and evaluation of Zn-doping

The GaN samples employed in this study were grown by vapor phase epitaxy with a method similar to the one reported previously [1, 24]. A two-zone furnace with a two inch diameter quartz liner was used. As is shown schematically in fig 1, we used a system where the NH_3 flow was introduced into the deposition zone in the opposite direction to the $\text{N}_2 + \text{HCl}$ gas flow. This was to ensure good mixing of these species for efficient GaN production. The purity of gases employed were $\text{HCl}:4\text{N}$, N_2 (carrier gas) $5\text{N}5$, and $\text{NH}_3:5\text{N}$, further $\text{Ga}:6\text{N}$ was always used. The only material used for crucibles and supports inside the two inch liner was quartz. This certainly causes inconveniences due to degradation of quartz in contact with GaN, but the use of e.g. alumina inside the furnace causes severe contamination with Al and Fe [25], which can interfere with Zn-doping. Substrates were always (0001)-oriented sapphire, since we found growth on this orientation to give smoother GaN layers, with properties superior to those grown e.g. on $(1\bar{1}02)$ -oriented substrates. The temperature of GaN deposition was held around 1025°C , suitable, growth rates were about $1\mu\text{m}/\text{min}$, which could be obtained by employing typical flow rates of 1.65 l/min for N_2 , 1.75 l/min for NH_3 and 0.20 l/min for HCl . Typical layer thicknesses were at least 15-25 μm , to avoid influence of the disordered region close to the substrate on the measured GaN properties.

Zn-doping was performed by introducing a quartz crucible containing Zn into the second separately regulated zone of the furnace, so that the main flow of N_2 and HCl passes over this Zn source (Fig 1). Zn is transported as Zn vapour and probably predominantly under our conditions of excess HCl, as $ZnCl_2$. Vapor pressures of Zn species in the growth area will be controlled by the setting of temperature of the separate zone containing the Zn crucible. With such an arrangement Zn-doping can be kept low ($< 10^{19} \text{ cm}^{-3} \text{ Zn}$), if the temperature of the Zn crucible was kept low enough ($< 400^\circ \text{ C}$), but doping of GaN in the range 10^{20} cm^{-3} is also easily obtained by keeping the Zn source at higher temperatures (e. g, $T_{\text{Zn}} \approx 650^\circ \text{ C}$).

The arrangement of introducing NH_3 into the deposition zone in the opposite direction to the carrier gasflow (containing N_2 and HCl) will give a peculiar spatial distribution of the front of the mixing zone. Since this mixing front is the most efficient place for GaN production, a separate study was made to map out its contours in the furnace. The mixing zone could be simulated at room temperature removing the furnace (Fig 1), which enables observation of the NH_4Cl formation upon introduction of the gases at the flowrates of normal GaN growth in the reaction tube. The resulting reaction picture is shown in Fig 2, and such contours of the mixing zone were very helpful in projecting the optimum position of substrates for GaN deposition in the furnace. It was found that the highest growth rates of GaN was obtained at the edge of the mixing front, and usually good growth behaviour could be observed over about 1 - 1.5 cm in horizontal direction from this edge. Further away into the mixing zone, growth becomes increasingly irregular, and finally polycrystalline. Undoped GaN layers show an increasing conductivity (N-vacancy concentration) in the same direction. Zn doping does not appreciably

change this growth behaviour. It was observed that the most favorable position for obtaining highohmic Zn-doped GaN was not at the reaction front but rather some distance into the reaction zone. A typical variation in resistivity was a factor 40 over a distans of 15 mm along the reaction zone. This behaviour can partly be explained by the variation of N-vacancy concentration in this growth direction, but also the mechanisms of incorporation of Zn into GaN could vary over this region. This will be discussed in more detail below under Sec IV.

Investigations with the SEM cathodoluminescence technique were performed to study homogeneity of Zn-doping. It was found, that for single crystalline layers of good surface topology, the Zn-related luminescence was continously spread out over the area of the wafers, indicating that Zn is incorporated rather homogeneously into the bulk of GaN. Variations in intensity over large areas was often observed, as is shown in fig 3. This intensity variation could indicate a variation in Zn concentration, but could also indicate a variable distribution of nonradiative center. As will be mentioned below in Sec III there are variations over large areas in the luminescent properties of the material, which may be related to the above SEM-observations.

The method of growth and Zn-doping described here seems to give a constant depth profile of Zn, i. e. the incorporation of Zn in GaN does not change over the period of growth, when no other parameters are changed. As an illustration to such behaviour is shown in fig 4 a Zn-profile of a GaN-wafer obtained by the SIMS-(secondary ion mass spectrometry) technique. This sample was actually an in-structure, i. e. a moderately Zn-doped low-ohmic n-type GaN layer, upon which a

high ohmic layer with higher Zn-concentration was grown. Higher Zn-doping was here achieved by momentarily moving the Zn source into a higher temperature region of the furnace. The result demonstrates the feasibility to grow such welldefined structures by this technique for LED applications.

For a detailed investigation of photoluminescence properties of Zn-related centers in GaN a number of samples doped with Zn in different concentrations were selected. The samples were investigated by the SIMS technique for the total concentration of Zn. The result for the samples to be mainly reported in this work are collected in table I. It was found that the Zn-concentration varied over nearly an order of magnitude in these samples. Also electrical data could be recorded for most of these samples by Hall measurements at room temperature by the van der Pauw-technique [26]. Measured values of mobility and resistivity of the samples are also included in table I. Note that the mobility decreases drastically upon Zn-doping in this range. Normal values of electron mobility in good undoped GaN layers grown under our conditions were around $150 \text{ cm}^2/\text{V.s.}$ The reduction with Zn-doping in the range $10^{19} \text{ cm}^{-3} - 10^{20} \text{ cm}^{-3}$ is therefore one to two orders of magnitude. This is a disadvantage in photoconducting applications of Zn-doped GaN, where usually high Zn-concentration is necessary to obtain suitable dark resistivity [6, 7].

III. Photoluminescence Data

III.1. General properties of Zn-related emissions

As was mentioned already in the introduction, different Zn-related PL spectra are observed when growth, doping conditions and temperature of observation are varied. In Fig 5 are shown some PL spectra

taken at three different temperatures with intrinsic excitation (Ar^+ UV-laser) from a GaN layer with rather high Zn-doping. Although at lower temperatures the blue 2.87 eV emission band dominates, the presence of additional PL emissions at lower photon energies is clearly demonstrated and these emissions even dominate at elevated temperatures in this particular sample (Fig 5). Such additional peaks are observed at about 2.6, 2.2, and 1.8 eV, but they are sometimes difficult to isolate from each other with above band-gap excitation. (The detailed analysis below under III:2 is partly made possible by the use of extrinsic selective excitation of the different emissions). In fact most previous studies of GaN light emitting devices of the m-i-n-type report electroluminescence emissions which do not peak in the blue spectral region, both blue, green, yellow and red colours have been reported [9, 13, 18, 19, 27, 28, 29]. The presence of several Zn-related centers as an explanation for such behaviour has previously been contemplated [8] but detailed investigations have so far only been carried out on the blue Zn-related emission [20].

We have tried to quantitatively correlate doping conditions and the occurrence of additional Zn-related emissions at photon energies lower than the 2.87 eV band. Our experience from measurements on many Zn-doped crystals is that a higher Zn-doping (say above the 10^{19} cm^{-3} level) causes the introduction of additional Zn-related impurity levels with higher binding energy. We have sometimes observed extreme cases where the red 1.8 eV emission dominates the PL spectrum of a highly Zn-doped crystal. In that case the PL intensity is often drastically reduced, due to an introduction of additional non-radiative recombination channels at high Zn-doping levels.

The different emissions introduced by Zn-doping of GaN also behave differently with excitation intensity. In Fig 6 is shown the total PL emission at 82 K over the wavelength region 1.7 - 3.3 eV for a rather heavily Zn-doped sample, excited with above bandgap radiation. It is observed that the higher energy emissions are relatively stronger at high excitation intensities. Consequently lowering the excitation intensity causes a relative enhancement of lower energy emissions. This is just another manifestation of the presence of several Zn-related centers, with different saturation properties. Similar observations are made when the temperature is varied, as shown in Fig 7 for the same sample as in Fig 6. At a higher temperature the high energy emissions are thermally quenched faster, as might be expected due to the lower binding energy of the corresponding Zn-levels.

III:2. Detailed investigation of different Zn-related emissions.

The blue Zn-related emission peaking at about 2.87 eV at low temperature (here called the A-band) is most easily accessible for a detailed study of emission properties, since it can often be studied without overlap with other emissions. Undoped GaN grown under our conditions usually show strong bound exciton spectra close to the bandgap (3.45 - 3.47 eV) at low temperature, in addition to a DA-pair emission at about 3.25 eV, replicated with 91 meV LO phonons [1]. Already a moderate Zn-doping [$< 10^{19} \text{ cm}^{-3}$] causes the bound exciton emissions to disappear, together with the DA-pair emission, so that the blue A-emission band completely dominates the PL spectrum. (This is in contrast to our observations on moderately Cd-doped GaN, where a similar blue emission is found to coexist with abovementioned higher energy features [1]. We have also observed (for the first time), in certain areas of such Zn-doped

crystals, a well-defined phonon structure on the envelope of the A-emission. In Fig 8 is shown a typical such curve obtained with above bandgap excitation. Clear phonon replica are observed with an energy of $\hbar\omega_A = 74 \pm 2$ meV. This energy is substantially smaller than the usually observed 91 meV LO-phonon, but is still in the optical phonon branch of GaN [30]. The observation of phonon structure proves the assignment of the broad A-emission to a phonon-assisted envelope due to lattice relaxation in the optical transition, and not to a broadened electronic level for the Zn state, as was previously sometimes suggested [20]. The A-emission has a long tail towards high photon energies, and can in our samples be detected up to 3.20 eV at 4.2 K. In most cases, however, the phonon structure is smeared out, and only the broad emission envelope is observed, as apparently was the case in previous studies of this emission [2, 8, 20]. The amount of spectral broadening was found to vary over the area of the crystal, and the phonon structure could therefore rather easily be wiped out if a focused excitation spot was not employed. Further, there is apparently a slight scatter in the position of the emission between different crystals, as shown in Fig 9. The entire emission envelope can be shifted as much as 25-30 meV between different crystals. Possible mechanisms to explain such behaviour will be discussed below under Sec IV.

The observation of discrete phonon replica for the blue 2.87 eV A-emission also makes possible a more detailed analysis of the electronic process involved in this emission. Assuming a linear model for the electron-phonon interaction, and further the validity of the Condon and mean value approximations, a very simple Poisson distribution of phonon replica $I_n \sim \frac{e^{-\lambda} \cdot \lambda^n}{n!}$ is expected for low

temperatures [22]. Here λ denotes the linear coupling strength, n is the order of the phonon replica. Using these assumptions a relatively simple discrete deconvolution method is available, to extract the purely electronic spectrum for the emission process [22]. The result of such a deconvolution treatment of the blue A-emission is shown in Fig 10. The resultant electronic curve is consistent with a linear coupling strength parameter $\lambda_A = 3.0 \pm 0.2$, and a Franck-Condon shift $\Delta_{FC} = \lambda_A \cdot \hbar\omega_A \approx 0.22 \pm 0.02$ eV for the A-center.

The so obtained electronic curve is very broad, a width > 100 meV (Fig 10), which is not expected for any simple recombination mechanism (DA-pair, free-to-bound transition, exciton recombination etc). It is therefore reasonable to suggest, that additional unresolved phonons are present in the optical spectrum. E.g. a mode $\hbar\omega_{A2} = 20$ meV with $\lambda_{A2} \approx 2$ would produce a much narrower no-phonon spectrum, as is shown in Fig 11, where the result of two consecutive deconvolutions of the A-emission assuming $\hbar\omega_{A1} = 74$ meV with $\lambda_{A1} = 2.8$ and $\hbar\omega_{A2} = 20$ meV with $\lambda_{A2} = 2$ is displayed. Although our choice of phonon energy $\hbar\omega_{A2}$ is somewhat arbitrary here, this assumption produces a physically reasonable no-phonon spectrum. Besides the temperature broadening behaviour of the A-emission described below under Sec III:3 seems to require such an additional mode. The total Franck-Condon shift for this A-center is therefore revised to $\Delta_{FC} = \sum \hbar\omega_i \cdot \lambda_i \approx 0.25 \pm 0.03$ eV.

The above data for phonon coupling parameters were extracted from the high energy part of the A-emission, for computational reasons. However, a convolution procedure [22], employing the extracted electronic spectrum and coupling strength, gives a spectrum in very good agreement with the experimental data for

the sample with the lowest Zn-doping (Fig 8).

In other crystals with a slightly higher Zn-doping, a discrepancy is observed between a convoluted spectrum for the A-emission and the measured spectrum, the latter showing an additional contribution on the low energy tail. This is due to the overlap with a new emission peaking at about 2.6 eV, with a high energy tail starting already at 2.9 eV. In Fig 12 such a case is illustrated, where also the difference between the measured spectrum and the A-emission part is displayed. Unfortunately we have not succeeded in obtaining conditions such that the B-emission appears dominant in any crystal investigated. The phonon structure for the B-emission can be observed in some areas of rather highly Zn-doped crystals but it is always interfering with similar structure from A- and C-emissions. The determination of the phonon energy for the main interacting mode is therefore less accurate than for the A-emission. We conclude a phonon energy $\hbar\omega_B = 80 \pm 5$ meV is involved in the B-emission. Since it was not possible to measure an accurate isolated spectrum for this emission, only a crude estimate of phonon coupling strength λ_B can be made from the observed width of the emission. We find λ_B to be similar to the A-emission, and ascribe a FC-shift $\Delta_{FC} \approx 0.25 \pm 0.04$ eV to the B-center.

In Fig 5 was shown a spectrum with an appreciable contribution from the green-yellow emission peaking about 2.2 eV (here called C-emission), present at rather high Zn-doping. In Fig 13 this emission has been obtained separately by using selective excitation (≈ 2.75 eV), and there it is evident that the high energy edge occurs around 2.6 eV. At particular points in the crystals phonon structure with a single

phonon energy $\hbar\omega_C \approx 84 \pm 3$ meV could be observed also for this emission, again proving that lattice relaxation is responsible for the width of these emissions. The magnitude of the FC-shift for this transition is of the same order as for the B-center, about 0.28 ± 0.04 eV, which is evident from a deconvolution procedure. The high energy tail broadening for this C-emission seems to be even more pronounced than for the A-emission discussed above.

A low energy red emission peaking at about 1.8 eV (Fig 14) was also found to be induced by Zn in our case, although in a previous work a similar emission was found to occur in undoped material [31]. This emission (here called D-emission) had a similar rather broad shape as the other emissions (A, B, C). No discrete phonon replica were observed for this emission and from its width we can only claim a FC-shift $\Delta_{FC} \approx 0.28 \pm 0.05$ eV, i. e. similar to the C-center. A search for possible additional emissions in the photon energy region $1.1 \text{ eV} < \hbar\omega < 1.7 \text{ eV}$ showed that no such emissions of intensities comparable to the above mentioned A - D-emissions were present in the Zn-doped material. We therefore conclude, that radiative levels introduced by Zn-doping are the four A-D levels described above. This appears to be in approximate agreement with recent data reported on Zn-doped GaN by another group [8].

III:3. Temperature dependence of PL emissions

III:3.1 Temperature quenching of emission intensities

The temperature variation of emission intensity has previously been reported for the blue A-emission by several authors [2, 20]. The overall impression from the collection of previous data is a large

variation observed between different samples [20]. In some cases temperature quenching has been found to be severe already above 100 K [31], in other cases quite good emission intensity could be maintained up to room temperature [2]. In Fig 15 are shown temperature dependences of PL emission intensities for the A-center from some of our Zn-doped crystals. It is evident from Fig 15 that the observed difference in activation energies for temperature quenching is appreciable, consistent with the overall picture from previous work. From our observations on many Zn-doped crystals it seems possible to classify the samples into two groups, one where a rapid quenching starts already above 100 K, another where good intensity persists up to room temperature. We believe that for the former group of samples the rather small activation energies observed for temperature quenching are not those related to the thermal release of carriers from the Zn-related centers (which has generally been assumed in literature). The concentration of additional nonradiative recombination centers in VPE-grown GaN can be substantial, dependent on the conditions of crystal growth [25]. In the latter case of a higher activation energy, we believe the observed data are not inconsistent with a thermal release of carriers from Zn-related centers.

As was noted above under Sec III:1, the lower energy Zn-related emissions associated with the B, C and D-levels often do have a temperature quenching that is associated with higher activation energies than for the blue A-emission. This is consistent with the fact that such emissions often dominate in the spectra from GaN

light emitting diodes at room temperature [28]. We have observed, however, that the temperature quenching of the C-emission intensity in some cases coincides with that of the A-emission in the case of low activation energy for the thermal process (upper curve in Fig 15). In such cases a common thermalization process for the two emissions seems to occur.

III:3.2 Spectral changes with temperature

The observations on the spectral behaviour of the Zn-related emissions A-D with temperature are important, because such variations can permit determination of the variation of the electronic level with temperature (shift of emission) as well as an independent check of evaluated phonon coupling strength (temperature broadening) [32]. The evaluation of such properties becomes very difficult for deep centers with sizeable phonon coupling in optical transitions, since very small shifts and broadening have to be observed on a broad emission envelope. In Fig 16 are shown PL emission curves for the blue A-center at several different temperatures. The extraction of the shift of the electronic level with temperature can approximately be done from the observed position of the envelope peak of the observed emission (broadening effects due to excitation of additional vibrational levels in the initial electronic state are in the first approximation important at the high energy wing only). It is observed from curves such as those in Fig 16, that the blue A-emission peak shifts about 15 ± 3 meV between 4.2 K and 295 K, significantly less than the corresponding bandgap shift [33]. However, very little shift is observed in the low temperature region, the total amount of the shift appears to start above 220 K. This is more readily demonstrated in Fig 17, where the discrete phonon replica of the A-emission are followed at different temperatures up to 190 K. Clearly no shift of the replica

is observed up to this temperature.

The broadening of the emissions with increasing temperature is more easily displayed when the peak positions are normalized, as was done in Fig 18. The broadening behaviour observed at the high energy edge can then be compared with theoretical curves obtained from a convolution procedure of the low temperature electronic spectrum [22]. Such curves are included in Fig 19. Clearly the experimentally observed broadening of the high energy wing of the A-emission is substantially larger than expected from a convolution of the 74 meV phonon mode alone, employing the same coupling strength λ_A obtained in the low temperature deconvolution procedure. This comparison is much improved by including also a second phonon mode $\hbar\omega_{A2}$ with $\lambda_{A2} \approx 2$ in the convoluted spectrum (Fig 19). This is a further support for the existence of such modes, as previously suggested from the above analysis of the A-emission spectrum. A broadening is also observed on the low energy edge at elevated temperature. This effect is simply due to overlap with lower energy emissions with a less pronounced temperature quenching (see above).

Corresponding data from a study of the B-emission peak could not be obtained, since this emission was hard to isolate from other Zn-related emissions (A- and C-emissions). The C-emission on the other hand, could be studied separately by selective excitation of about 2.75 eV. In Fig 20 are shown such curves for 77 K and 293 K. The curves exhibit a shift of the peak position to lower energies of about 30 ± 5 meV between 4.2 K and 293 K. The broadening of the high energy edge is also here found to be substantially larger than expected from convolution of the about 84 meV $\hbar\omega_C$ -mode alone. This is shown in Fig 21 as the difference in high energy edge between 77 K and

293 K, when the latter curve is shifted 30 meV towards higher energy to overlap at the peak and at the low energy wing. The theoretically expected broadening is smaller than the one experimentally observed in this case. A second lower energy phonon mode would improve the agreement, as for the A-center. No corresponding reliable data on temperature broadening were obtained for the red D-emission in this work.

IV Discussion

IV:1 Incorporation of Zn-centers in relation to growth parameters

It appears as Zn has been by far the most popular dopant studied in VPE-grown GaN during the last decade [2, 6-10, 12, 20, 21, 31, 34, 35]. This is not suprising, since it can be incorporated in the material in large quantities, and therefore would be a prime candidate for achieving low-ohmic p-type conductivity. The requirement would be that Zn is introduced mainly as a shallow acceptor, while at the same time the concentration of donors, such as the V_N , is kept low. The collection of experimental data on Zn-doped GaN available in literature so far give a disappointing picture from this point of view. Low-ohmic p-type GaN has not been observed with Zn-doping (or any other doping for that matter). High resistive material was, however, obtained in many cases, indicating the introduction of acceptorlike centers by Zn-doping.

As pointed out in the introduction a more detailed study of the growth parameters for GaN is necessary before its defect-related properties such as luminescence and electrical behaviour can be controlled. Unfortunately previous investigations, in a different experimental apparatus, often do not allow a meaningful comparison for details in the VPE-crystal growth and the defect incorporation.

E.g. in some systems (as in our case), the NH_3 flow enters the deposition zone in the opposite direction from the HCl and GaCl flow, in which case a very complicated spatial distribution of optimum mixing conditions is obtained, while others have used a geometry where all gases were introduced from one direction [25]. As mentioned above under Sec II the choice of growth parameters for a particular run can easily produce a wide spectrum of GaN properties (single crystalline or polycrystalline, low resistive or high resistive), dependent primarily only on the position of the substrate in the deposition zone. A systematic study of variations of GaN properties with position in the deposition zone is possible (and has been obtained in our case), but can obviously not easily be compared with previous results from other workers [25], even though the main parameters, such as temperature or partial pressures of different reactants, are quite similar.

It is therefore not surprising, that different laboratories have reported rather large variations in properties of Zn-doped material, even though the total amount of Zn incorporated was probably similar [36]. In fact, our results on rather highly Zn-doped material clearly show the existence of four different radiative Zn-related levels in material grown at $1030^\circ - 1050^\circ \text{C}$. In material grown under conditions reported to be quite similar in another laboratory, essentially only the blue emitting A-center was observed, although at least as much Zn was reported to be incorporated as in our case [20], and similar growth rates were employed. Further we easily obtained high resistive GaN material by such Zn-doping, while the authors of Ref 2 did not. It seems clear that the obtained distribution of Zn between different centers is critically dependent on parameters other than the Zn partial pressure at a particular temperature of growth. E.g. recent

data by a third group on Zn-doping of GaN predict that high-ohmic material would be very difficult to obtain at 1050°C in their apparatus [8]. This is in contradiction to our results, as reported above. Another striking difference between our observations and those reported in Ref [8] is that in our case it was found easier to obtain high-ohmic Zn-doped GaN at lower growth rates, while the opposite was claimed in ref [8]. In both cases excess p_{HCl} was employed. One conclusion that can be drawn from the experiences on our particular growth apparatus, is that the reaction kinetics for the formation of different Zn-related defect levels (A-D) depends critically on the growth parameters. As was noted above, it seems clear that details in the growth procedure other than the total concentration of Zn introduced determine the relative abundance of different Zn levels A-D. Since in our system all material was necessarily grown under excess p_{HCl} , we assume the Zn is transported to the mixing zone mainly as ZnCl_2 , but to some extent as free Zn. Some reduction of ZnCl_2 to Zn is expected to occur upon entering the mixing front, due to the increased partial pressure of hydrogen p_{H_2} caused by GaN formation. If the incorporation of Zn in the GaN is primarily a surface reaction, one might anticipate that Zn would choose different lattice sites if it arrives at the surface as Zn atoms or if Zn comes from a reaction with ZnCl_2 at the surface. Another factor that is probably important is the N-vacancy concentration, which in turn seems to be closely related to the growth rate [37]. As noted above under Sec II, the highest growth rate, which occurs closest to the reaction front, favours a low V_{N} concentration in undoped layers [37], and also low resistive Zn-doped layers. High resistive Zn-doped layers are more easily obtained further away from the reaction front, where undoped layers show a higher V_{N} -concentration (lower growth rate). If the N-vacancies are

involved in the incorporation of Zn into centers causing high resistive GaN, this relation would indeed be expected.

There seem to be a few general conclusions that are common to our observations and those of other investigations. At low Zn concentration there seems to be a general agreement that the blue-emitting A-level is the only level that is introduced. A high Zn-concentration seems to be a necessary condition for obtaining appreciable concentrations from the B,C and D levels giving other colours in emission. This condition, however, is not sufficient to guarantee the occurrence of these levels, as shown by some of our data, but also by the results of Ilegems et al. [2]. Clearly cases have been observed where only the radiative A-center has been observed, in spite of high doping [2]. We have also observed a general correlation between the occurrence of additional radiative B, C and D levels and the compensation of the material (high resistivity). This does of course not necessarily mean that all these three levels (B-D), or even any of those, are directly involved as compensating centers. We shall return to the question of the possible identity of these centers in more detail below.

IV:2 Discussion of radiative transitions

Our rather detailed analysis of the emission properties of GaN:Zn has revealed, apart from the existence of four different Zn-related levels, that the broad emission bands are envelopes of phonon replica of broadened electronic transitions. It appears as this was generally not realized in earlier work, where the width of the emissions was attributed to either band tailing [20] or concentration gradients [34]. Indeed, for such deep levels in III-V-compounds

a fairly strong lattice coupling is expected in optical transitions, if one compares with similar observations on other III-V-compounds [22].

Previous discussion of the mechanisms of radiative transitions involved for Zn-doped GaN have mainly been concentrated on the A-center [20], with some exception [8]. E.g. it has been concluded, that the blue A-emission arises from transitions from tail states in the conduction band to a broadened Zn acceptor level, i. e. a free to bound transition [20]. The main argument was an observed peak shift with excitation intensity, which however, was not observed by us or by other workers [21, 31], and therefore probably due to some overlap with the B-emission. Boulou et al. have recently concluded that all the observed emissions A-C are distant DA-pair emissions, from observations of spectral shifts in excitation dependence and of nonexponential decay behaviour. On the contrary we do not observe any significant shift of emissions A and C with excitation intensity, apart from what can be explained by different intensity dependence of overlapping emission bands. A non-exponential decay could alternatively be explained as caused by the release of carriers from traps, as was found e. g. in photoconductivity data [7]. The analysis of a 2.4 eV peak in GaN:Zn reported by Matsumoto et al. [34] is clearly influenced by a superposition of spectra from both B-level and C-level. We believe that the experimental data on Zn-related emissions A-D in GaN, including the data presented in this paper, are not sufficiently clear to permit a definite conclusion about the radiative mechanism. Generally it seems like broadening effects are so strong, that relevant features of the electronic (no-phonon) transitions are obscured. The arguments for a DA-pair

mechanism presented by Boulou et al. are certainly acceptable, and their data for the blue A-emission could possibly be related to ours, if it is assumed that their Zn-concentration was much lower. If one compares with the better established emission at about 3.25 eV in GaN (at low temperature) there seems to be little doubt that this is a conventional DA-pair emission involving a shallow donor (≈ 30 meV) and a moderately shallow (≈ 225 meV) unidentified acceptor. In that case it is expected, and indeed also observed, that this shallow donor will show thermalisation effects already at rather low temperatures, leading to a shift to a free-to-bound spectrum. For the 3.25 eV emission this is clearly manifested by the appearance of two peaks in the temperature range 50-120 K, where the high energy (free-to-bound) peak dominates, the higher the temperature. If the Zn-related emissions A-D were to be dominated by a similar DA-pair process, the same common shallow donor (believed to be the N vacancy) would be expected to be involved. Therefore a shift to the FB transition would certainly be expected in the same temperature range as for the 3.25 eV DA-pair system. No such shift with rising temperature could be observed in our data. It must be recognized, however, that the details of the distant pair model are not expected to apply for Zn-concentrations of the order $10^{19} - 10^{20} \text{ cm}^{-3}$. Substantial broadening of the shallow donor level is expected in this case. The position of the electronic peak for the A-emission deduced in Fig 11 allows an estimate of the A-level binding energy. If we assume the donor levels are effectively broadened into a band, connected with the conduction band, a broadened shape like the one in Fig 11 is reasonable. A peak at 3.10 eV at 4.2 K would then correspond to a binding energy of about 0.37 eV for the A-level, if we assume the donor band tail is centered around a 30 meV binding-energy [1]. A more detailed discussion on binding energies

for the A-D levels will be given separately in connection with data for optical cross sections for these levels [23].

As noted above, we believe no firm suggestions of detailed models for radiative transitions should be done from the present data, which are still too seriously affected by broadening effects. In the following we shall therefore only use a schematic picture of the A-D emissions, as being transitions from the conduction band (including shallow donor band tails) to Zn-related acceptor states A-D. In principle contributions from excitons bound to complex Zn-centers similar to e.g. the Zn-0 center in GaP [38, 39] cannot be excluded, but our data do not suggest any such effects. We believe this general picture of the Zn-related levels A-D as acceptorlike levels is well supported by independent data on electrical compensation or photoconductivity response [6, 7].

IV:3 Broadening behaviour

As apparent from the presentation of experimental data on radiative spectra for Zn-related levels A-D in Sec III above, there are mainly two different broadening effects that occur on optical spectra. One is a broadening of the electronic spectra, which occurs even at the lowest temperatures, and which in many cases is strong enough to wipe out any phonon structure in the observed emission envelope. The second major effect is a temperature broadening of all spectra, which is expected in the CC-phonon model of lattice relaxation upon optical transitions [32]. It is simply due to the optical transition from thermally excited higher vibrational levels in the initial vibronic state to the final vibronic state levels.

Several mechanisms can be suggested which cause broadening of electronic spectra, most of them would be more important in highly doped material. For donor concentrations exceeding about 10^{19} cm^{-3} the interimpurity distance in GaN is well below the Debye screening length, and donor levels are broadened or even merged into the conduction band. We believe this effect could be one reason why we do not observe any shift between DA-pair and FB-transitions in our luminescence spectra, as discussed above. A donor as shallow as about 30 meV would broaden very easily. Further the effect of charged impurities in general do perturb band edges locally, which effectively contributes to broadening in optical spectra. The concentration of dislocations in the material is unknown, but experience from other III-V-compounds grown under similar conditions indicate that a very large dislocation density is expected to be inherited from the substrate-GaN interface, even though the thickness of the material is 50 - 100 μm , i. e. most of the interface strain is released. It is possible that Zn would tend to be partly pinned to dislocations, in which case certainly a shift in the position of its energy level would be expected due to a local disturbance of bonding states close to the dislocation. The built in strain, finally, is in itself another cause of broadening. The rather large differential thermal expansion coefficient between GaN and the sapphire substrate causes severe strain during cool-down, which is partly relieved by cracking of the material (mostly the sapphire), at GaN thicknesses exceeding 30-50 μm . A residual strain would cause a strain-induced splitting of impurity related energy-levels, and also a small shift in the energy position of the level. A local distribution of residual strain would evidently be an important broadening mechanism for impurity related spectra. It is not possible to establish which of the above mentioned mechanisms

are most important, as long as the nature of radiative transitions at these high doping levels are not known.

Unfortunately the more shallow emissions (excitons bound to shallow centers and shallow DA-pairs) are very efficiently quenched in our Zn-doped GaN. For shallow bound excitons it is reasonable that binding cannot occur at high densities of charged point defects. The reason for the quenching of the 3.25 eV DA-pair emission is less obvious. One possible explanation would be that the 3.25 eV emission is associated with the Ga-vacancies, which might then disappear to a large extent upon Zn-doping, if Zn enters on Ga-sites when forming the A-level. Another possibility is that the capture cross section for holes of the Zn A-level is much larger than for the shallower 0.225 eV level associated with the 3.25 eV emission in GaN. Since no emission close to the bandgap could be observed, we do not know whether the high concentration of Zn would have some effect on the bandgap of GaN, or the observed shift of the Zn-emissions (Fig 9) is related to some other effect of the high doping concentration. It is of course also possible to imagine a concentration effect on the impurity binding energy, but since bound state wavefunctions for these deep centers are extremely localized in real space, we believe even a doping in the range $5 \cdot 10^{19} \text{ cm}^{-3}$ would be marginal to cause a shift of 15-30 meV as observed. Note, however, that the absolute values determined for the total Zn-concentration are uncertain by a factor 5.

Turning to the observed broadening with temperature of the emissions (notably A- and C-emissions, Fig 18-20), we observe a substantially larger broadening than expected below 293 K, if we only account for the established presence of the high energy CC phonon mode ($\hbar\omega_A \approx 74 \text{ meV}$, $\hbar\omega_C \approx 84 \text{ meV}$). As shown in Fig 11 the introduction of a second linear

mode of lower energy results in a reasonable electronic spectrum for the A-emission. The existence of lower energy modes is certainly not unreasonable, e. g. for the deep O donor in GaP two modes of 48 meV and 19 meV respectively build up the emission envelope [22]. Due to the large electronic broadening effects in the case of GaN:Zn, replica due to such a mode, even if it was perfectly sharp in energy, would be extremely difficult to detect on the high energy wing of the emission spectrum. Further a low energy mode, such as the $\hbar\omega_{A2}=20$ meV mode suggested above with $\lambda_{A2} \approx 2$, will qualitatively produce the experimentally observed temperature broadening effect, even for temperatures below 100 K (Fig 18).

Our description of phonon coupling is based upon a linear CC-phonon interaction, i. e. the same phonon energies and coupling strengths are used in phonon emission as well as in phonon absorption. This is not experimentally proved, since clear phonon replica were not resolved below the zero phonon line or in absorption spectra corresponding to these emissions [23]. A linear CC-phonon coupling model was found to be strictly valid for the deep O-center in GaP, however [22]. A possibility which has also been neglected is the occurrence of a Jahn-Teller splitting of such deep acceptor levels, which would complicate the phonon coupling treatment. Such problems are not expected for shallow acceptor centers in GaN, due to the non degeneracy of the valence band top [33, 40], compared e. g. GaP [41]. For deep centers one can not easily predict degeneracy, however, in particular if the detailed identity of the center is unknown.

Similar arguments on phonon broadening seem to apply to the C-emission. The broadening is in this case also considerably in

excess of the calculated effects of a linear 84 meV phonon alone. Introduction of a lower energy phonon mode seems also here as a natural explanation of observed excess broadening with temperature, as well as in the electronic spectrum. This would only slightly alter the estimated FC-shift for the C-level, say $\Delta_{FC} = 0.28 \pm 0.04$ eV.

IV:4 Considerations on the identity of Zn-related centers in GaN

From the previous discussion it is clear, that the detailed nature of the four Zn related levels A-D could not be revealed in the present study, mainly due to the high doping range necessary to obtain optical spectra from all these four levels. We consider the possibility that these levels should not be Zn-related to be quite small. In this connection it should be mentioned, that a broad peak centered at 2.15-2.2 eV has been reported in GaN not doped with Zn by several authors and believed to be related to intrinsic point defects [42, 43]. Similar emissions around 1.7 eV (i.e. rather close to our D-emission peaking at about 1.8 eV) have been reported in material not doped with Zn. Since such emission were so weak that they could not be detected in our material when they were not deliberately doped with Zn, we consider the connection with Zn of all emissions A-D reported here to be quite firm.

Data on electrical compensation discussed above under Sec II can be easily explained, if the A-center is associated with Zn on Ga sites (Zn_{Ga}), while the levels B-D are all associated with Zn on N sites (Zn_N). We note the Zn on N-sites might be capable of binding up to three electrons, while at the same time it removes a V_N donor, i.e. a very efficiently compensating acceptor [7]. The simplest model to suggest is then that the A-center is simply the substitutional Zn_{Ga}

acceptor, and that the centers B-D correspond to the three different charge states of the same center Zn_N . Some previous authors have argued that Zn_Ga is shallower and is active in the shallow 3.25 eV DA-pair emission in GaN [2]. This pair emission peak appears at approximately the same position irrespective of what acceptor is the dominating dopant [2]. The small deviations of the peak positions (typically a few meV) observed between differently doped samples can easily be accounted for by the dependence of the pair emission envelope on doping level and excitation conditions [44, 45]. As was pointed out previously, it seems very unlikely to us that no central cell shift should occur among different acceptors in GaN. It is true that the variation in binding energy for shallow excitons bound to neutral acceptors in GaN is rather small between different doping conditions. It should be noted, however, that no strict "Haynes rule" for the connection between bound exciton binding energies and the corresponding acceptor binding energies can be expected for such materials. In fact it has recently been found for ZnTe, that all excitons bound to neutral acceptors have very similar binding energies, while the corresponding acceptor binding energies can be very large and do vary within large limits [46]. Therefore it seems more natural to suggest, that the only Zn-related level observed at low doping is the Zn_Ga -level, and also the A-level we observe. We see no reason why the Zn_Ga -level should not be observable at all in optical spectra. On the other hand, from the present data one cannot exclude, that complexes involving Zn_Ga , such as e. g. $\text{Zn}_\text{Ga}^\text{V}_\text{N}$, could be more abundant than the Zn_Ga centers. An important question that remains to be solved is then the origin of the shallow 0.225 eV acceptor causing the shallow 3.25 eV DA-pair emission in GaN. It seems like this is the most shallow acceptor observed so far in GaN,

and the above suggestion of its connection with V_{Ga} needs further experimental support. The proposed connection of levels B-D with a Zn_{N} center also deserves a critical discussion. From a simple Coulomb-potential binding scheme one would predict, that the binding energy for these levels would increase in the order Zn_{N}^{-} , $\text{Zn}_{\text{N}}^{2-}$ to $\text{Zn}_{\text{N}}^{3-}$. Since observed binding energies are large (0.6-1.4 eV) the potential is certainly dominated by contributions of non-coulomb origin. Exchange and correlation terms are also expected to be large. Therefore it seems at present extremely unsafe to predict the ordering of the three levels in the bandgap of GaN (for this model we assume that all three ionization levels occur in the bandgap). Consequently it is not possible to correlate the dominance of different emissions B-D under different doping with a proposed level scheme. An argument for the Zn_{N} center is that just three additional radiative centers (besides the A-center) are observed on Zn-doping, no additional emissions were found at lower photon energy. The observed low radiative efficiency when these levels dominate the spectrum is easily explained for a center holding more than one charge carrier with a simple nonradiative Auger process competing with the radiative process for the level [47]. At the highest concentration of Zn we believe excitation transfer between nearby centers can easily occur, to additionally lower the radiative efficiency of recombination for all centers in the material. The simple model for the A-D levels as being acceptorlike levels associated with Zn_{Ga} and Zn_{N} suggested above, apparently does not seem to be in disagreement with available data for GaN:Zn. Certainly other possible models should not be excluded at the present time, alternative models for levels B-D could e.g. involve different complexes with Zn and V_{N} , as proposed by Boulou et al. [48]. Such a

model would predict that the A-center is of a similar origin as B-D levels, however [48].

IV:5 Applicability of Zn-doping for GaN devices

To summarize, the results on Zn-doping of GaN presented so far, do not seem to predict that Zn is an acceptor dopant that would solve all the problems in making attractive light-emitting devices from GaN. It should be noted, that quite good radiative efficiencies have been obtained with Zn doping (Ref 13, and also in our laboratory) employing so called in-structures, i. e. an insulating Zn-doped GaN layer on top of n-GaN. For large scale application it is felt, however, that pn-junctions are needed. As noted above the most shallow Zn-related A-center occurs at about 0.37 eV. This would make it difficult to produce low-ohmic p-type GaN with Zn-doping, in particular since at high doping levels Zn apparently prefers to partly occupy much deeper states B-D. If our suggestion that the B-D levels are connected with V_N is correct, a very important task would be to explore growth conditions for a low V_N concentration, to avoid the problem of a very high compensation for p-type material. The problem of selfcompensation upon acceptor doping of GaN is not clarified from the presently available experimental data, but theoretically a quite low enthalpy of formation is predicted for the N-vacancy [50, 51]. As noted above, a more shallow acceptorlike state exists in GaN, notably the one involved in the commonly observed 3.25 eV DA-pair emission. The definite identification of this acceptor faces the task of careful impurity analysis of the material, in correlation to growth conditions [25]. It has recently been revealed, that dominant acceptors in other similar rather ionic materials, such as ZnSe and ZnTe, are not those connected with native defects [49],

and therefore the realization of low-ohmic p-type material in e.g. ZnSe is contemplated as quite feasible. The situation could be similar for GaN, certainly the concentration of a large number of impurities in the material grown by the present VPE-technique seems to be at ppm levels [25]. An effort towards a refined growth technique might therefore give a material of considerably higher potential for applications (such as blue-emitting LED:s) than presently available.

V Conclusions

Results are presented from a study of Zn doping in GaN, at the rather high doping levels $10^{19} - 10^{20} \text{ cm}^{-3}$ relevant for presentday LED-devices from such material. A growth geometry different from the one used in previous studies was employed, with the NH_3 gas flow entering from a direction opposite to the main $\text{N}_2 + \text{HCl}$ flow in the furnace. Studies of the total Zn-concentration incorporated into GaN by the SIMS-technique indicate a fairly homogeneous distribution of Zn in single crystalline material grown on [0001]-oriented substrates. The incorporation of Zn was found to be critically dependent on growth conditions. Electrical compensation of normally n-type GaN occurs most easily at a reduced growth rate, i.e. under conditions of an increased V_N production rate.

Our data reveal that Zn doping of GaN introduces four different deep acceptorlike states A-D. It appears that a low concentration of Zn tends to favour the production of the most shallow A-center. At higher concentrations of Zn it seems like the deeper B-D levels are introduced most efficiently into material grown under conditions of high V_N production. There seems to be a correlation between the occurrence of

these additional B-D levels and the achievement of electrical compensation. The apparently different electrical compensation behaviour between the A level and the B-D levels together with optical data suggest a tentative identification of the A-level as the substitutional Zn_{Ga} -center, and the B-D levels as the Zn_{N} -center, having three different charge states.

Detailed photoluminescence data reveal characteristic broad emission bands peaking at about 2.87 eV (A), 2.6 eV (B), 2.2 eV (C) and 1.8 eV (D) for the four Zn-related levels A-D. The large halfwidth of these emissions (0.35 - 0.40 eV) was found to be due to phonon cooperation in the optical transitions, produced by lattice relaxation upon change of charge state of the defect levels. A principal phonon mode of energy $\hbar\omega_{\text{A}} = 74 \pm 2$ meV, $\hbar\omega_{\text{B}} = 80 \pm 5$ meV, $\hbar\omega_{\text{C}} = 84 \pm 3$ meV was directly observed for emissions A-C. Corresponding linear coupling strengths $\lambda_{\text{A}} - \lambda_{\text{C}}$ were found by a deconvolution procedure to be slightly less than 3 for these emissions A-C. An analysis of the electronic lineshape was also performed. Consistent results are obtained if in addition to the above principal modes an unresolved lower energy phonon mode is also active in optical transitions. Very similar Franck-Condon shifts were evaluated for these levels $\Delta_{\text{FC,A}} = 0.25 \pm 0.03$ eV, $\Delta_{\text{FC,B}} = 0.25 \pm 0.04$ eV, $\Delta_{\text{FC,C}} = 0.28 \pm 0.04$ eV and $\Delta_{\text{FC,D}} = 0.28 \pm 0.05$ eV.

All luminescent spectra are affected by strong electronic broadening effects, mainly due to the high doping levels employed. An analysis of the deconvolved A-emission reveals a binding energy of the A-level as $E_{\text{A}} = 0.37 \pm 0.04$ eV at 4.2 K. For the levels B-D only approximate binding energies as $E_{\text{B}} = 0.65 \pm 0.08$ eV, $E_{\text{C}} = 1.02 \pm 0.05$ eV and

$E_D = 1.43 \pm 0.08$ eV can be estimated from luminescence spectra alone. Temperature broadening effects studied for the A and C emissions give a reasonable quantitative agreement with theoretical expectations from a linear coupling two mode model, employing the same phonon energies and coupling strenths as in the deconvolution of the low temperature spectra. The shift of the electronic levels with reference to the conduction band between 4.2 K and room temperature was estimated to be only about 15 meV for the A-level, and somewhat larger or about 30 meV for the C-level.

It is concluded that the difficulties to achieve low-ohmic p-type GaN by Zn-doping are partly due to the high binding energies of Zn-related acceptor levels, but also to the possible connection of Zn-levels B-D to N-vacancies. An upgrading of the present growth procedures for GaN to avoid chemical contaminants on the ppm levels seems to be necessary before definite conclusions can be drawn on the feasibility of preparing low-ohmic p-type GaN.

VI Acknowledgements

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Figure captions.

- Fig 1 Schematic picture of growth apparatus used in VPE-growth of GaN on sapphire. Note that the NH_3 flow is introduced in the opposite direction to the main flow ($\text{N}_2 + \text{HCl}$). The Zn source was placed in a separately temperature stabilized zone of the furnace.
- Fig 2 Photograph of the spatial extent of NH_4Cl - formation at room temperature in the quartz system used for GaN growth, for flow rates of NH_3 (introduced from right) and $\text{N}_2 + \text{HCl}$ (introduced from left) similar to those used in GaN growth. NH_4Cl appears as suspended small white particles, in the picture, and the behaviour of the mixing front observed in this case gives a good indication of the proper position for substrates in an actual GaN growth at elevated temperatures.
- Fig 3 Cathodoluminescence topograph (a) of an area of a Zn-doped VPE-grown epitaxial GaN-layer, showing large area variations in Zn-related luminescence intensity. The corresponding SEM surface picture of the same area is shown in (b) for comparison.
- Fig 4 Concentration profile for Zn^{64} in an in-structure of GaN measured by SIMS, showing a reasonably constant Zn-concentration with depth from surface in the region of lower doping (towards the substrate). The higher concentration

close to the surface corresponds to the highly Zn-doped (insulating) region obtained by shifting the Zn-source to a higher temperature. The gradual change in Zn-concentration observed closer to the surface is mainly an effect of the finite time for temperature rise for the Zn load (from $T \approx 350^{\circ}\text{C}$ to $T \approx 625^{\circ}\text{C}$).

Fig 5 Photoluminescence spectra at three different temperatures for a rather highly Zn-doped GaN layer excited with the 3511 Å + 3514 Å lines of an Ar^+ laser. Relative intensities are shown as experimentally obtained.

Fig 6 Photoluminescence spectra at 82 K for a rather highly Zn-doped GaN-layer, measured at three different excitation intensities of wavelengths 3511 Å + 3514 Å. (Intensities are normalized). Clearly low energy emissions are relatively stronger at low excitation intensities.

Fig 7 Photoluminescence spectra of the same Zn-doped GaN layer as in Fig 6 for three different temperatures 82 K, 172 K, and 292 K, excited with above bandgap photon energies (3511 Å + 3514 Å). The intensities shown are normalized. Low energy emissions are favoured at the higher temperatures.

Fig 8 Photoluminescence spectrum at 4.2 K of a moderately Zn-doped GaN-layer, showing almost only the blue A-emission, peaking at about 2.87 eV. Above bandgap excitation (3511 Å + 3514 Å) was employed.

- Fig 9 High energy part of photoluminescence spectrum at 4.2 K for two different, rather highly Zn-doped GaN layers, obtained with above bandgap excitation (3511 Å + 3514 Å). A clear shift of 25 - 30 meV is observed between the two curves.
- Fig 10 High energy part of photoluminescence spectrum from a Zn-doped GaN layer, obtained at 4.2 K with above bandgap excitation (——). Also shown is a deconvoluted spectrum (...) obtained from the experimental curve by employing a linear phonon coupling strength $\lambda = 3$ with $\hbar\omega = 74$ meV.
- Fig 11 Electronic (no-phonon) spectrum for the A-emission, obtained by a second deconvolution procedure with $\hbar\omega_{A2} = 20$ meV and $\lambda_{A2} = 2$ (---). The upper curve is the result of the primary deconvolution step, obtained with $\hbar\omega_{A1} = 74$ meV and $\lambda_{A1} = 2.8$. A no-phonon peak at about 3.10 eV is obtained by this procedure.
- Fig 12 Photoluminescence spectrum at 4.2 K (——) for a GaN layer with a slightly higher Zn-doping than the one used for Fig 8. Also shown is the expected contribution of the A-emission to this spectrum (---), obtained by a convolution procedure. This curve (---) is similar to the one shown in Fig 8. The approximate spectral distribution of the overlapping B-emission on the low energy wing is also shown (.-.-.-.).

- Fig 13 Photoluminescence spectrum for the same GaN layer as in Fig 12 at 4.2 K, obtained by selective low intensity excitation at about 2.75 eV. Under these conditions only the C-emission is observed.
- Fig 14 Photoluminescence spectrum for a rather highly Zn-doped GaN layer at 293 K, excited with above bandgap radiation (3511 Å + 3514 Å). The main peak observed is the D-emission. The approximate shape of the high energy edge of this emission (---) was obtained from a subtraction of higher energy emissions with well-known spectral behaviour.
- Fig 15 Photoluminescence intensity for the A-emission measured for two different Zn-doped samples for different temperatures up to room temperature. Measurements were done with above bandgap excitation (3511 Å + 3514 Å). Intensities are normalized to the level 1000 at 4.2 K. The result shows the large variation in activation energies for the non-radiative processes occurring for Zn-doped GaN.
- Fig 16 Photoluminescence spectra for the A-emission in a rather lightly Zn-doped GaN layer, measured at four different temperatures (5 K, 80 K, 180 K, and 293 K) with above bandgap excitation (3511 Å + 3514 Å). Relative intensities are those obtained in the measurements.
- Fig 17 Selected part of photoluminescence spectra for a Zn-doped GaN layer at four different temperatures (4.8 K, 80 K, 170 K, and 190 K). The curves are vertically shifted with a depressed zero level for easy comparison.

- Fig 18 High energy part of photoluminescence spectrum for the A-emission in Zn-doped GaN measured at seven different temperatures, using selective below bandgap excitation (3800 Å). Curves are drawn only for the lowest (5 K) and highest (290 K) temperatures. All spectra are normalized to the same peak intensity, and the 290 K curve was shifted 15 meV to compensate for the shift in A-level binding energy at this temperature.
- Fig 19 High energy edge of the blue A-emission in Zn-doped GaN at two different temperatures, 4.2 K (a) and 293 K (d), the latter shifted 15 meV towards higher energies. The intermediate curves b and c are the results of a theoretical convolution procedure to obtain the effect of phonon-induced broadening at 293 K, employing one phonon ($\hbar\omega_{A1} = 74$ meV, $\lambda = 3$, curve b) resp two phonons ($\hbar\omega_{A1} = 74$ meV, $\lambda = 2.8$; $\hbar\omega_{A2} = 20$ meV, $\lambda_{A2} = 2$, curve c).
- Fig 20 Normalized photoluminescence spectra for the C-emission in a rather heavily Zn-doped crystal obtained with selective excitation (2.75 eV) at two different temperatures 77 K and 293 K). A shift of 30 ± 5 meV towards lower energies is clearly observed.
- Fig 21 Normalized photoluminescence spectra for the C-emission in the same crystal as in Fig 20 at 77 K and 293 K respectively, measured with selective excitation (2.75 eV). The 293 K curve is shifted 30 meV towards higher energies to display more clearly the effect of temperature broadening.

Sample	Zn conc. [cm^{-3}]	ρ [Ωcm]	μ [cm^2/Vs]
Zn I	$3.1 \cdot 10^{19}$	$3.8 \cdot 10^{-2}$	4.1
Zn II	-	1.5	0.1
Zn III	$8.2 \cdot 10^{19}$	0.18	1.4
Zn IV	-	-	-
Zn V	$1.5 \cdot 10^{20}$	-	-
Zn VI	$1.5 \cdot 10^{19}$	$2.7 \cdot 10^{-2}$	12.6

Table I

Summary of data for Zn-doping and electrical properties of the epitaxial GaN layers referred to in this paper. Note that Zn concentration could not be obtained on sample II, due to its small size. Sample IV was a Zn-doped in-structure, and was too high resistive for electrical measurements, as was also the case with sample V.

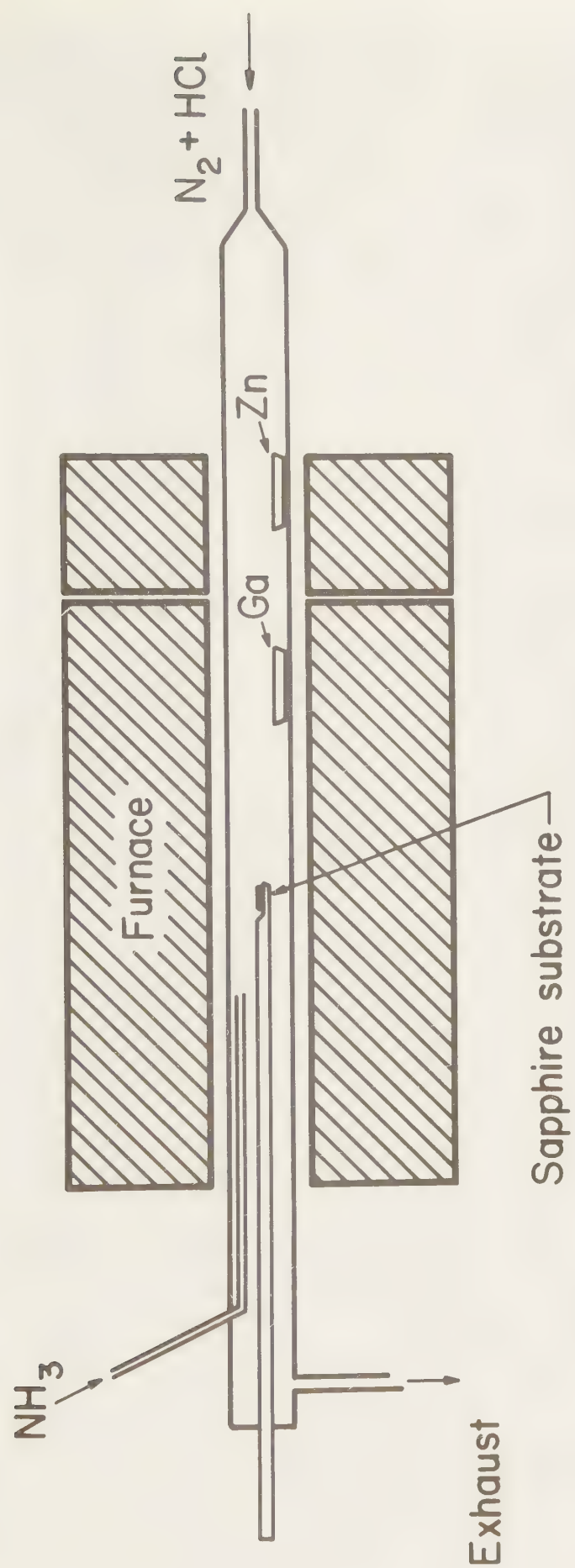
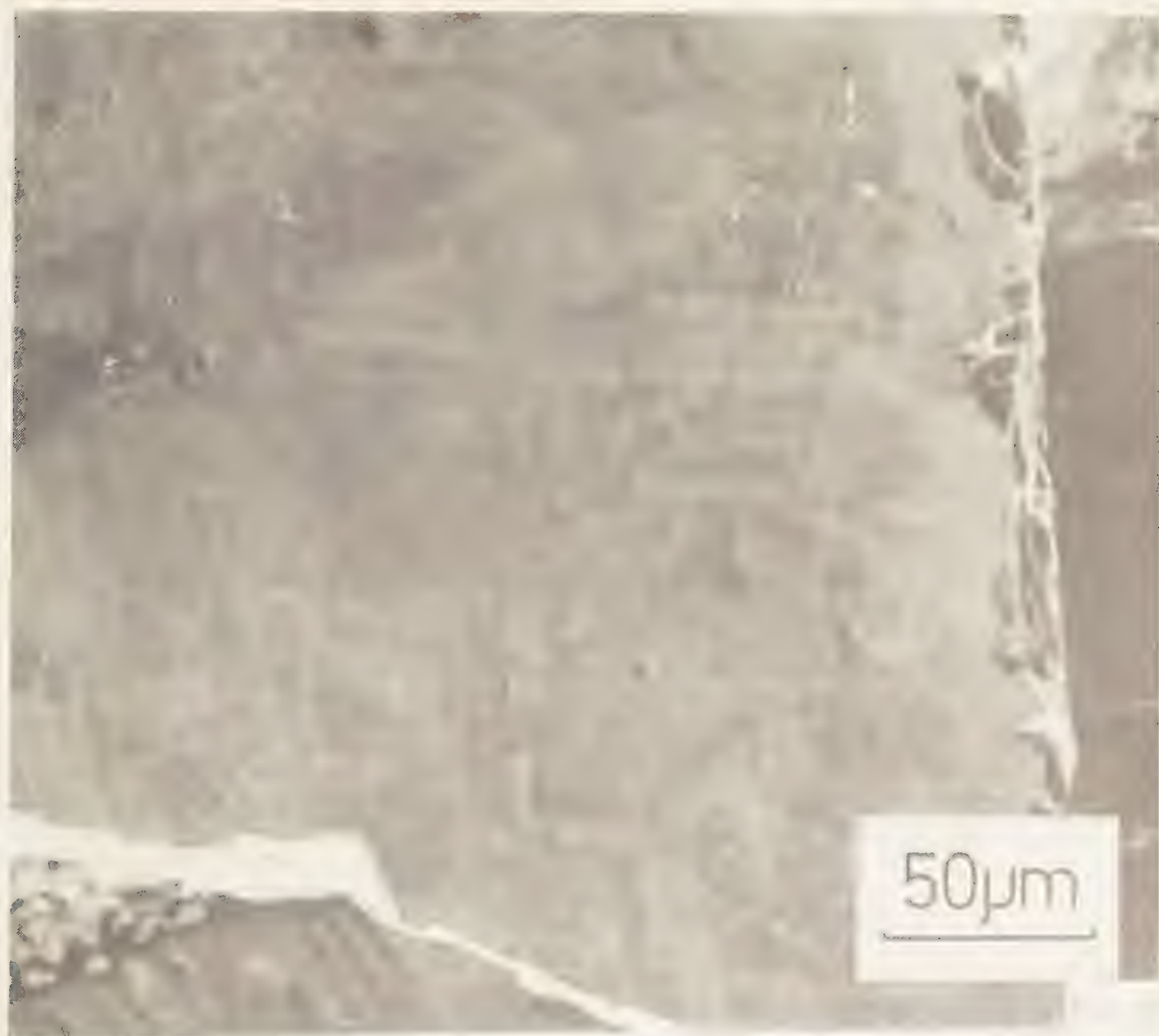
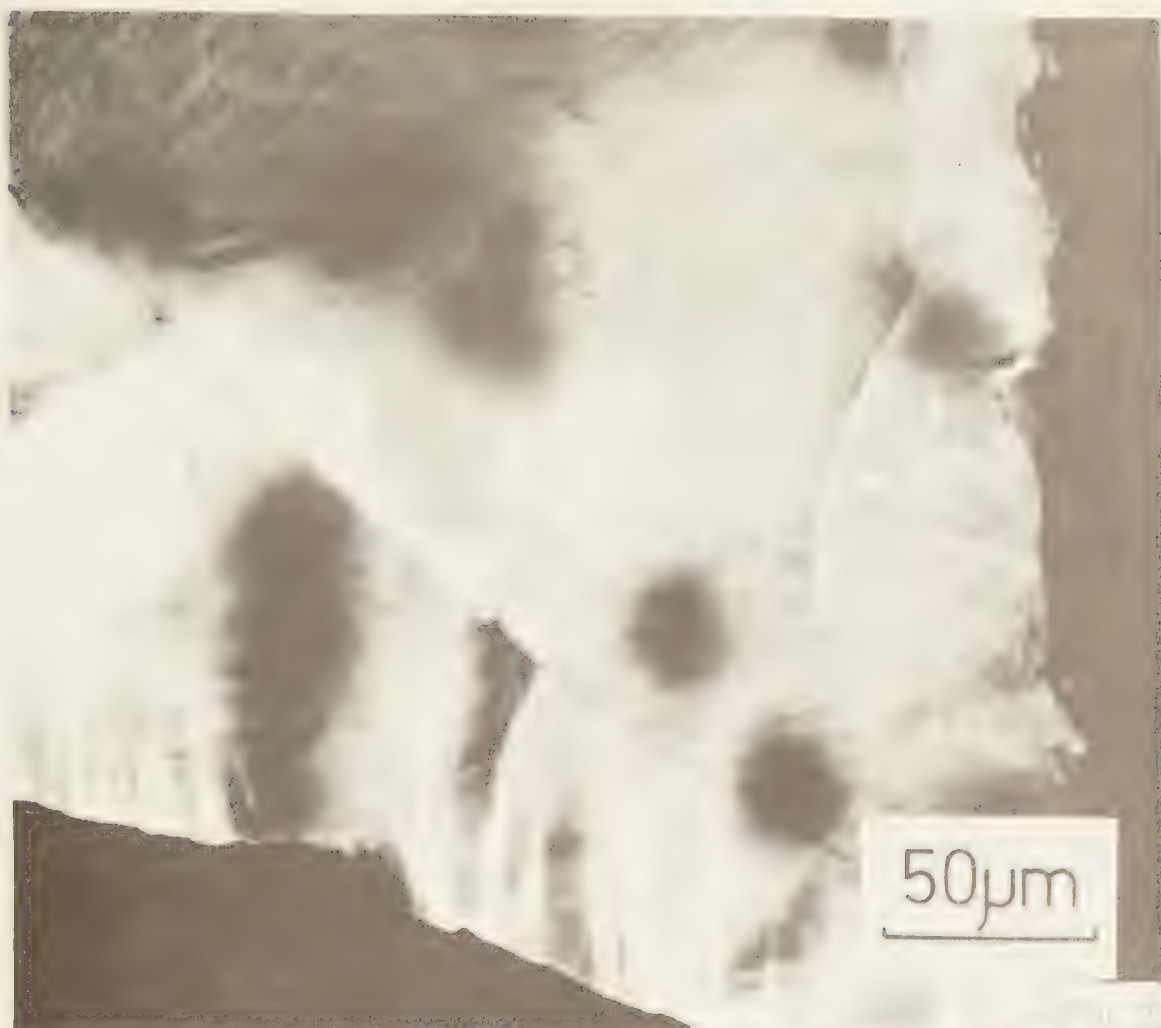


Fig. 1





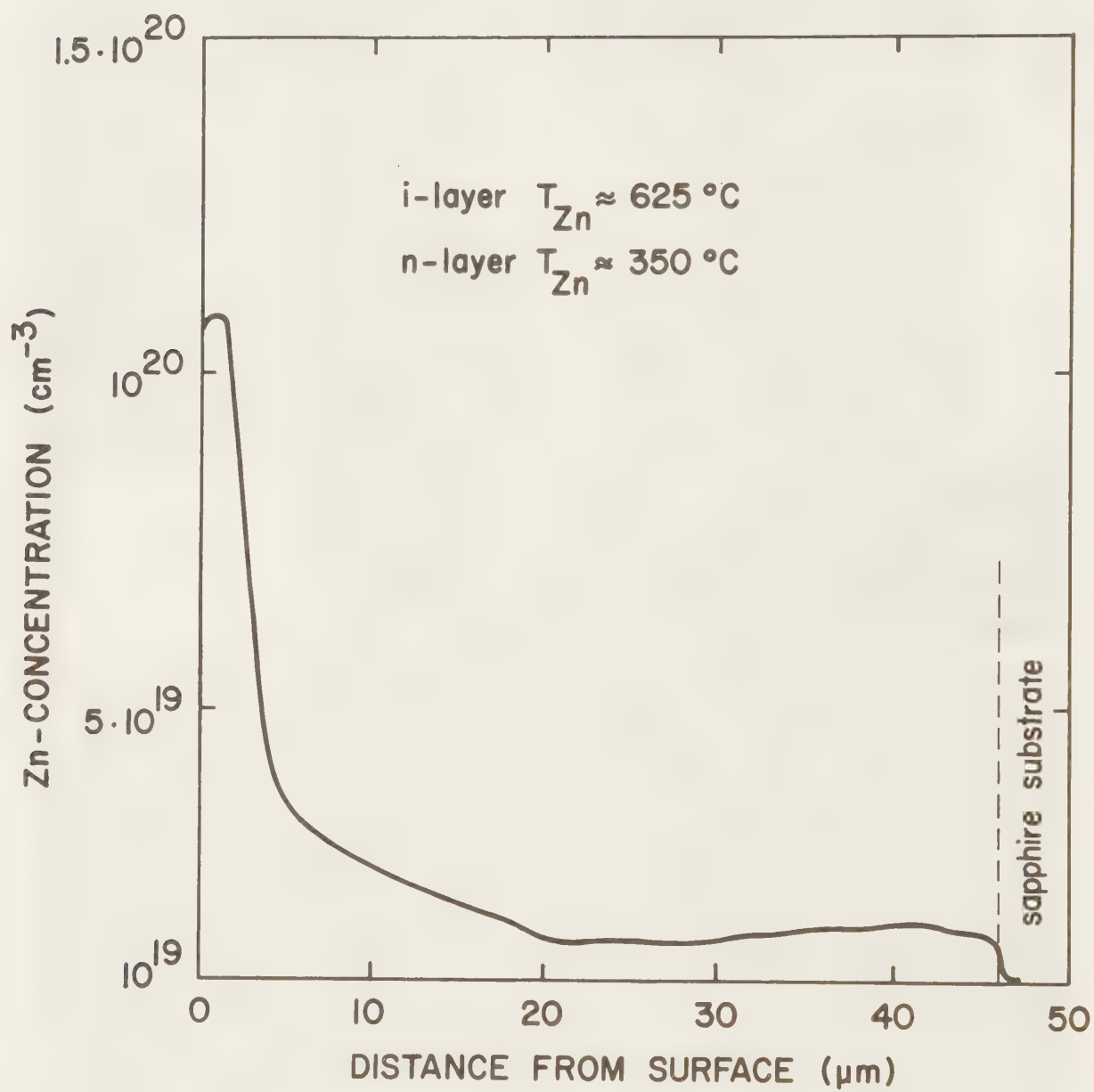


Fig.

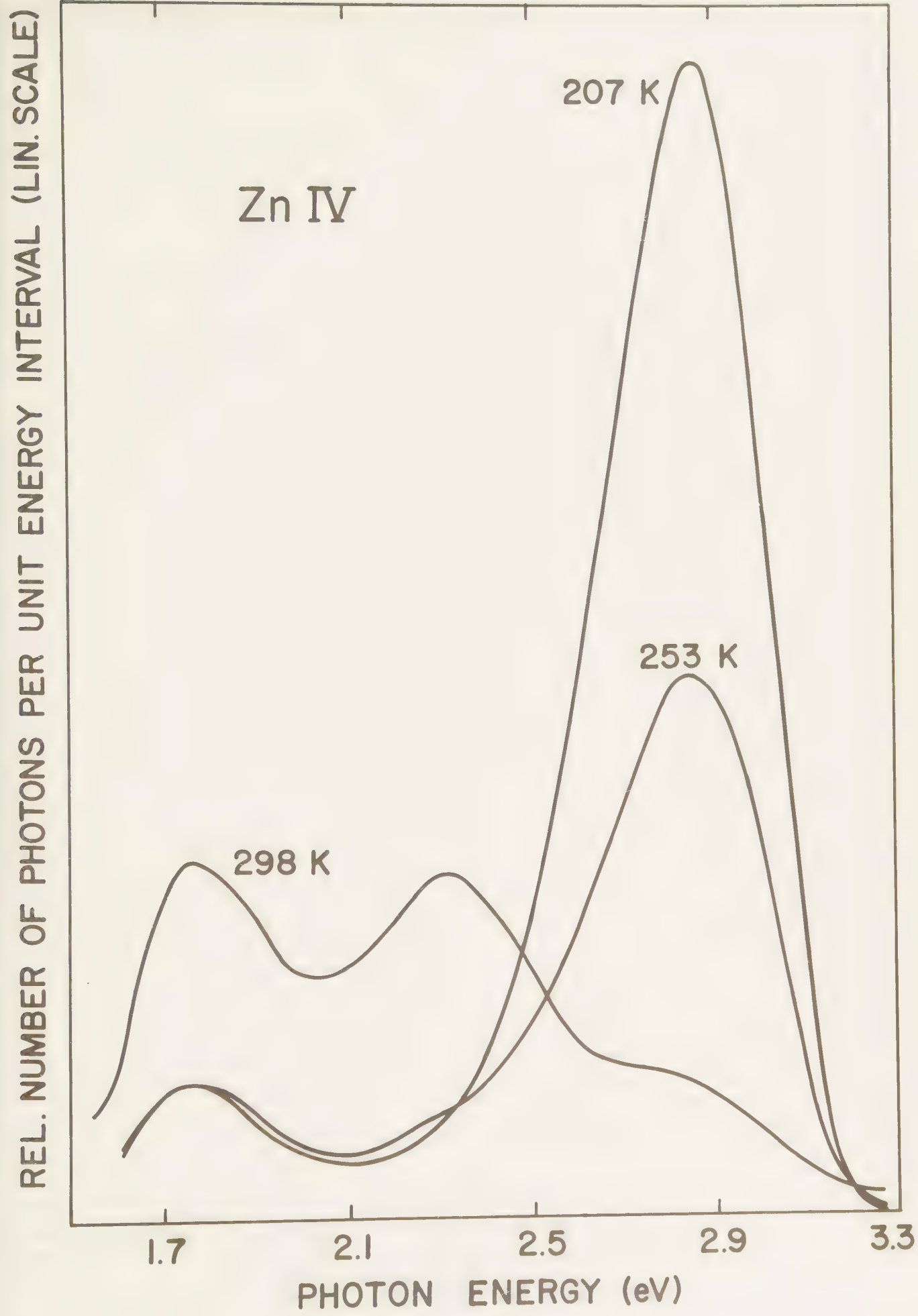


Fig. 5

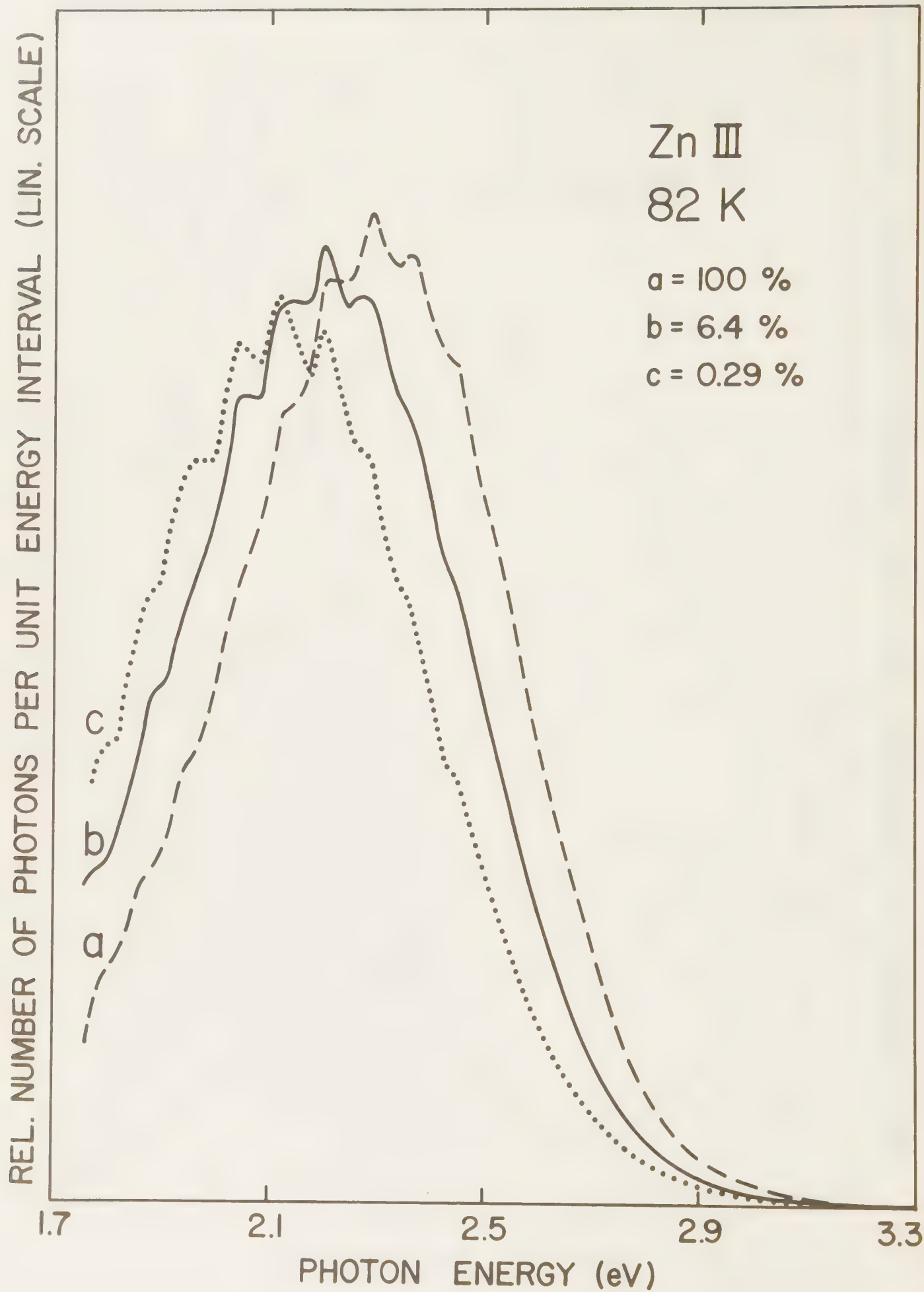


Fig. 6

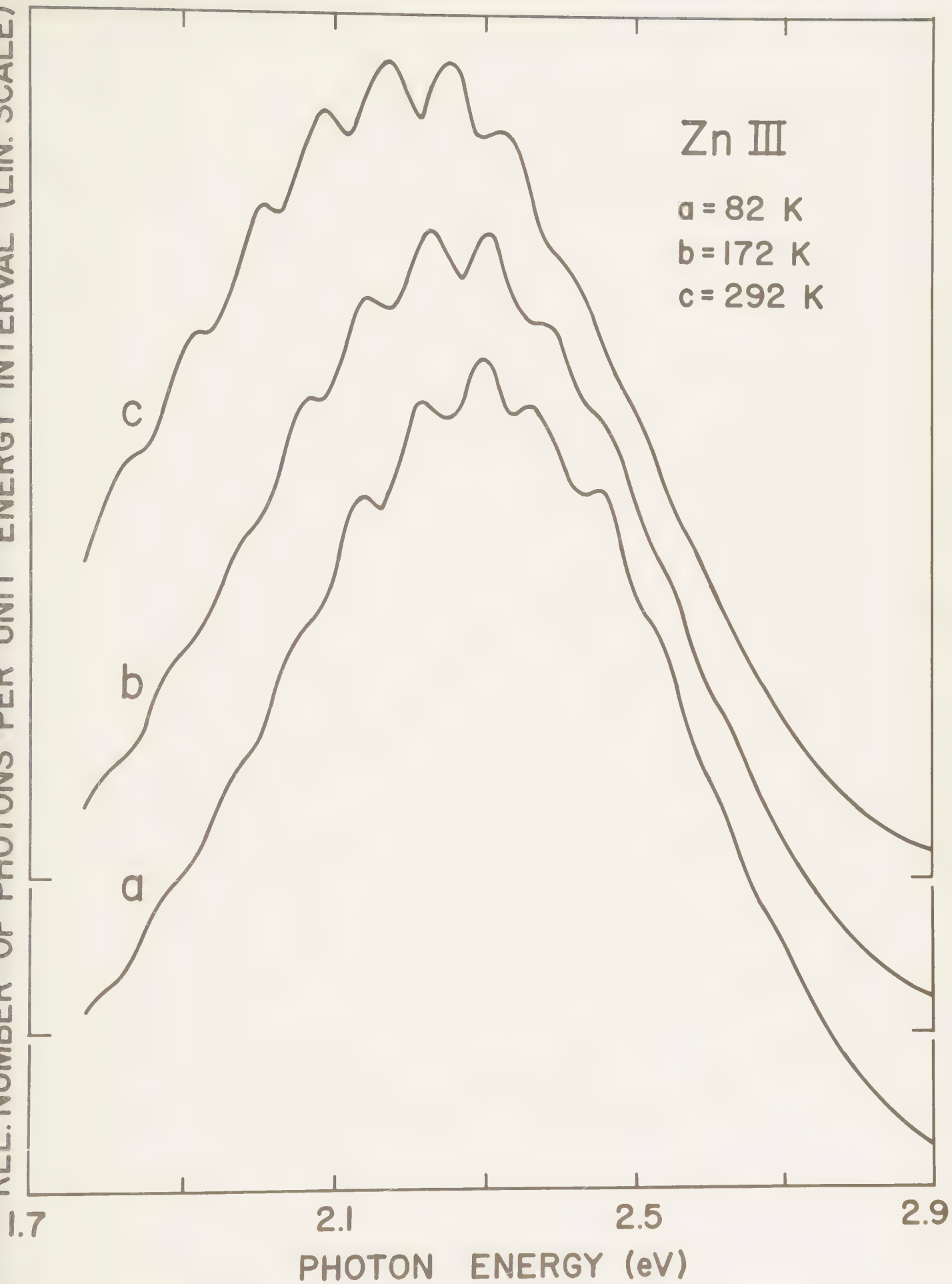


Fig. 7

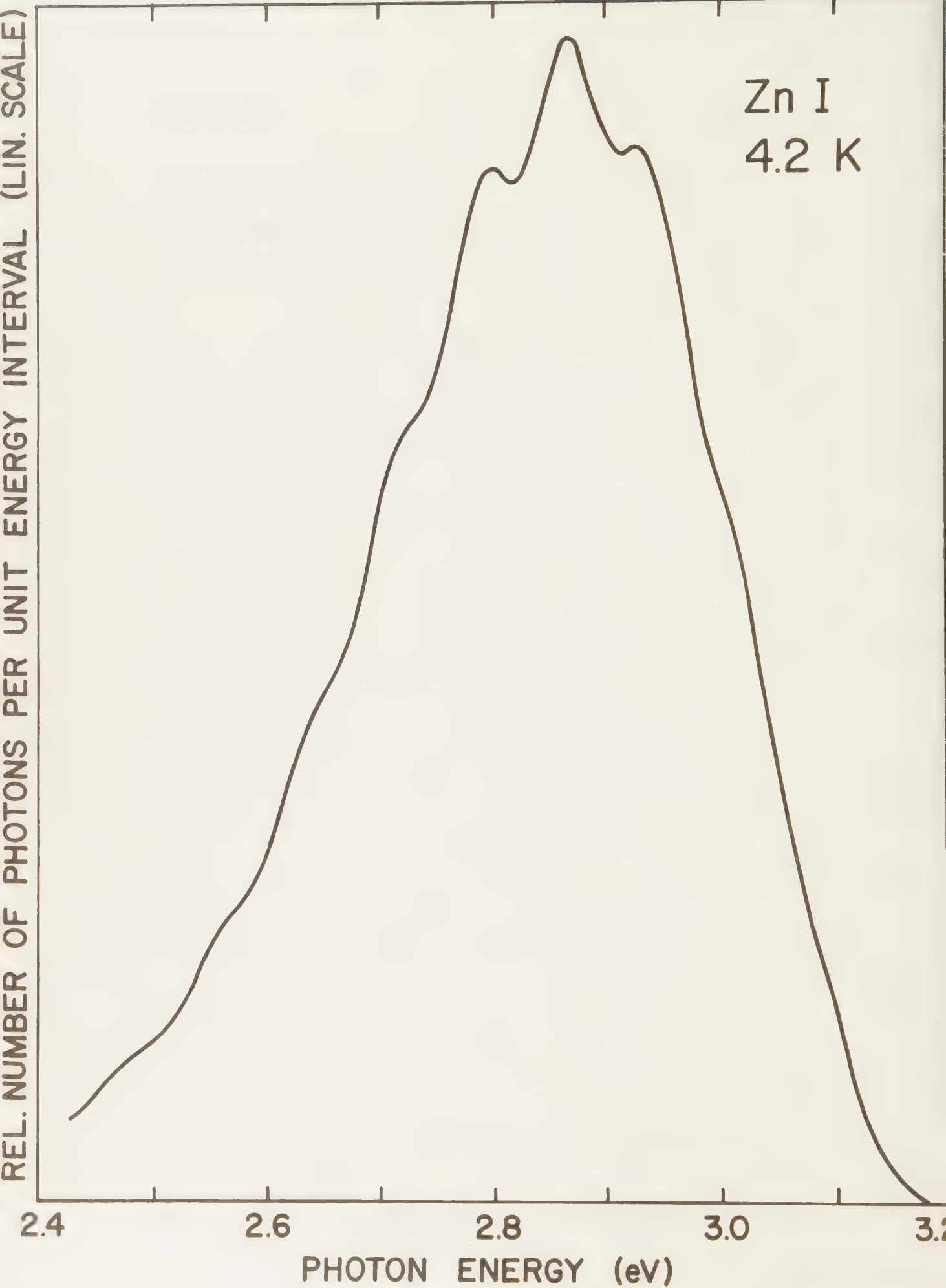


Fig. 8

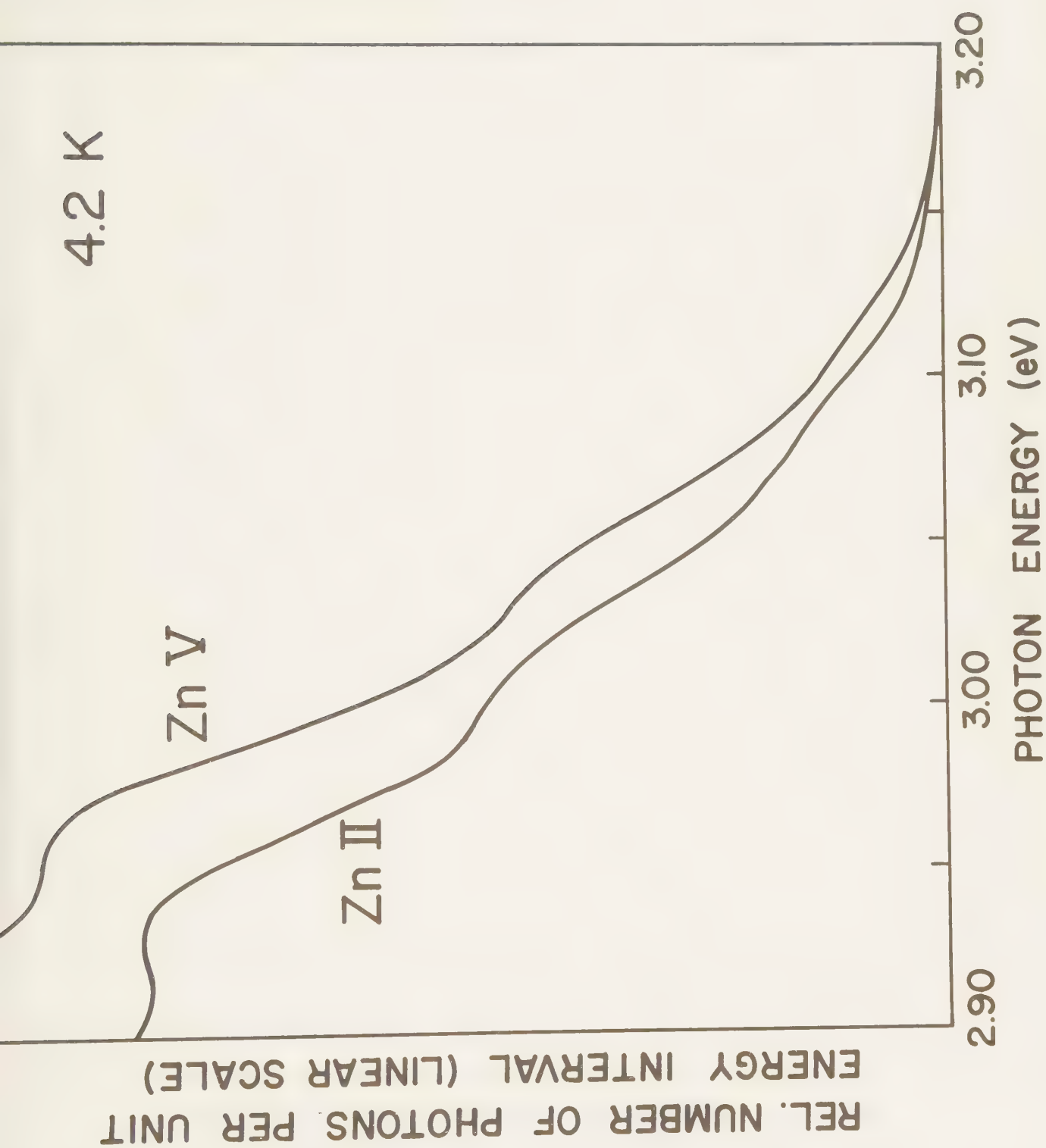
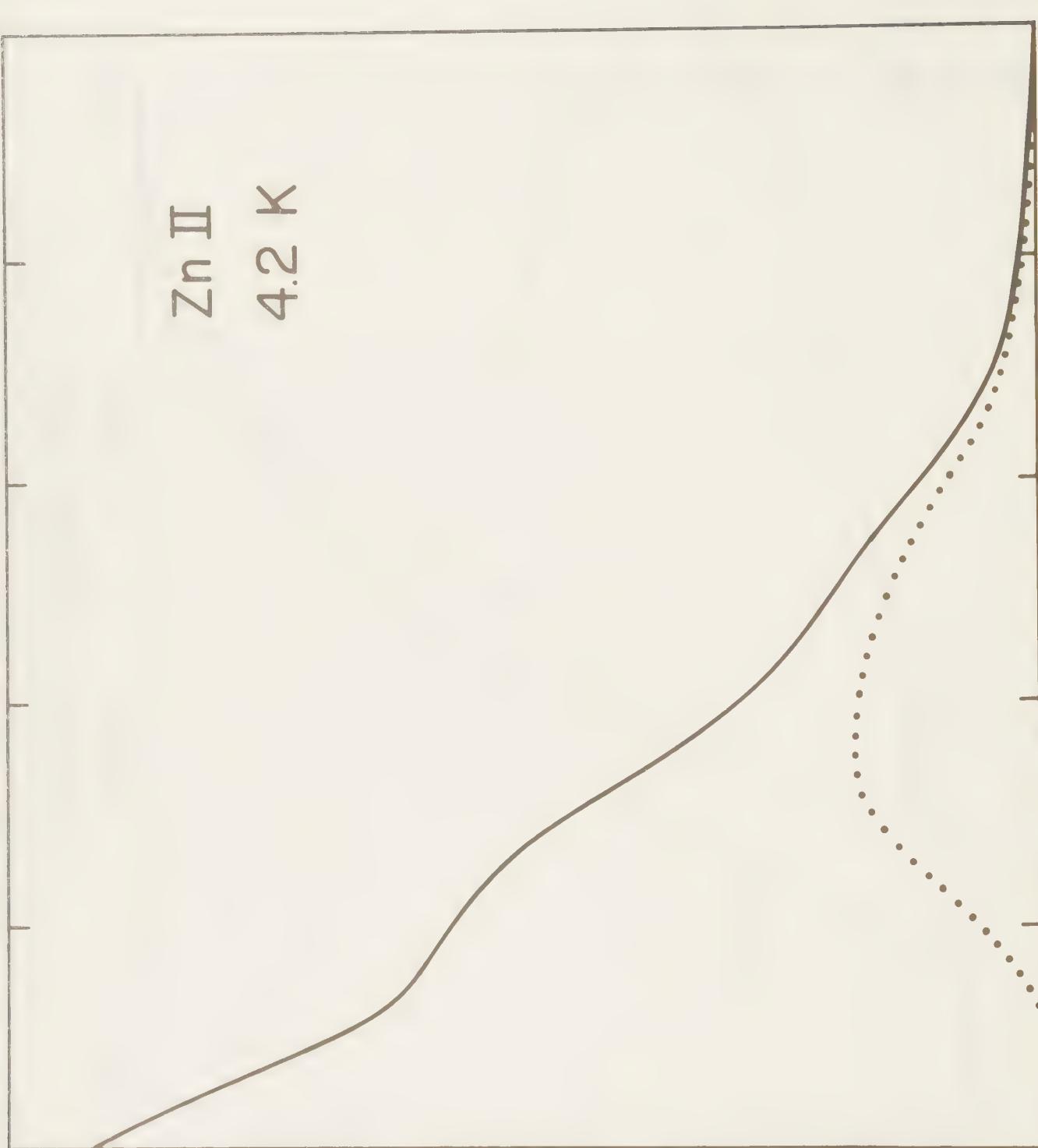


Fig. 9

REL. NUMBER OF PHOTONS PER UNIT
ENERGY INTERVAL (LINEAR SCALE)

Zn II
4.2 K

3.20
3.15
3.10
3.05
3.00
2.95
PHOTON ENERGY (eV)



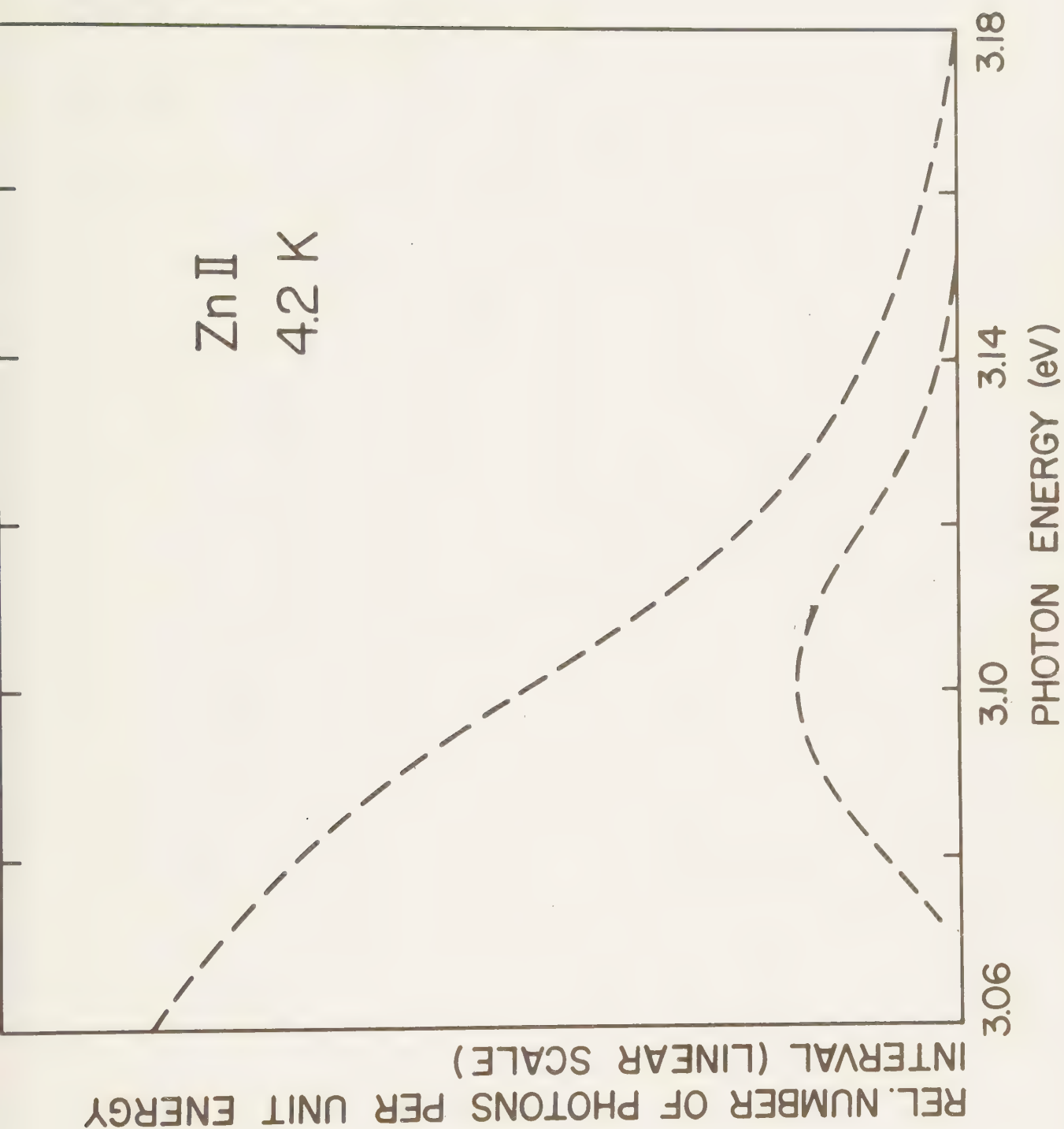
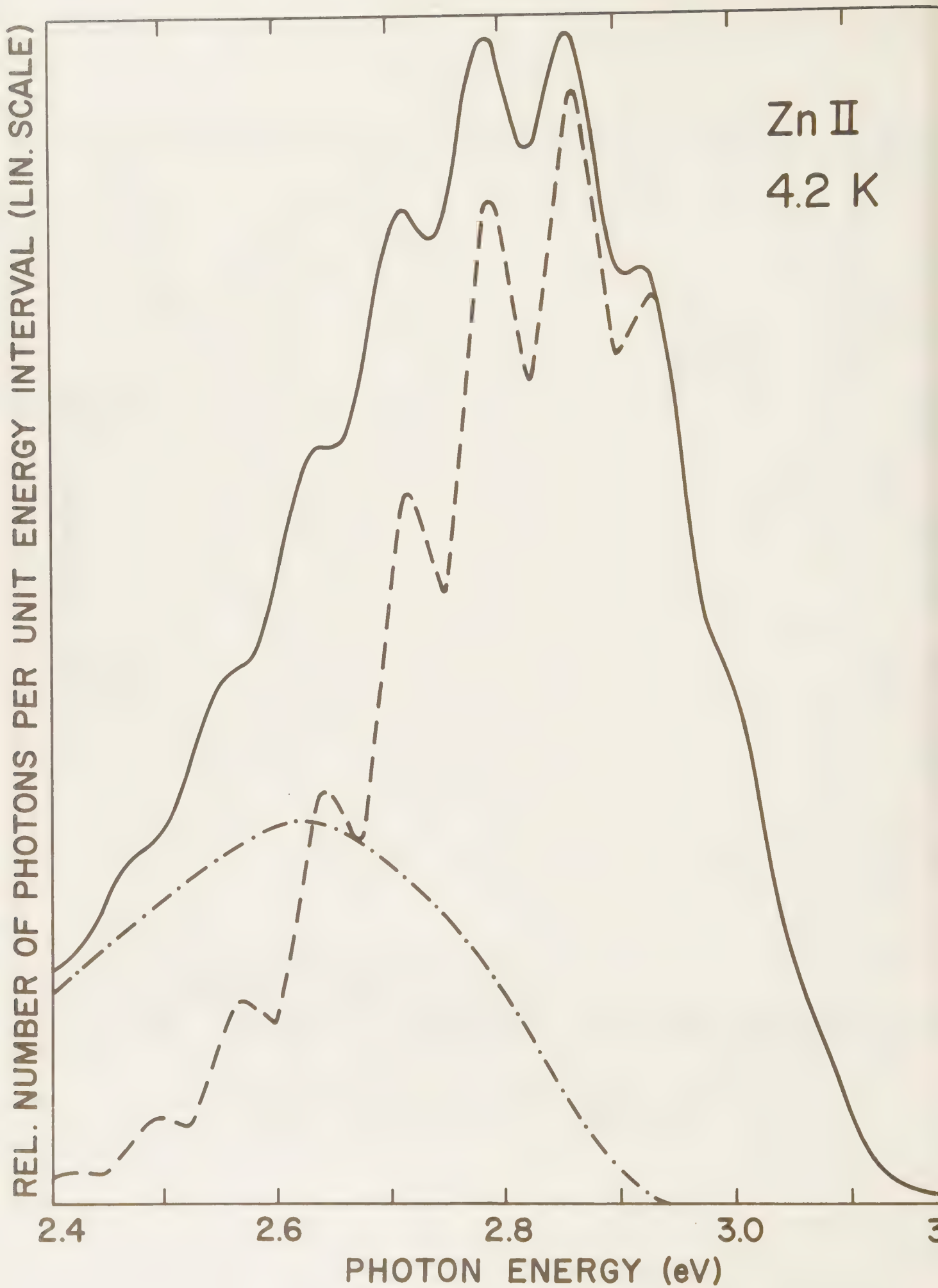


Fig. 11



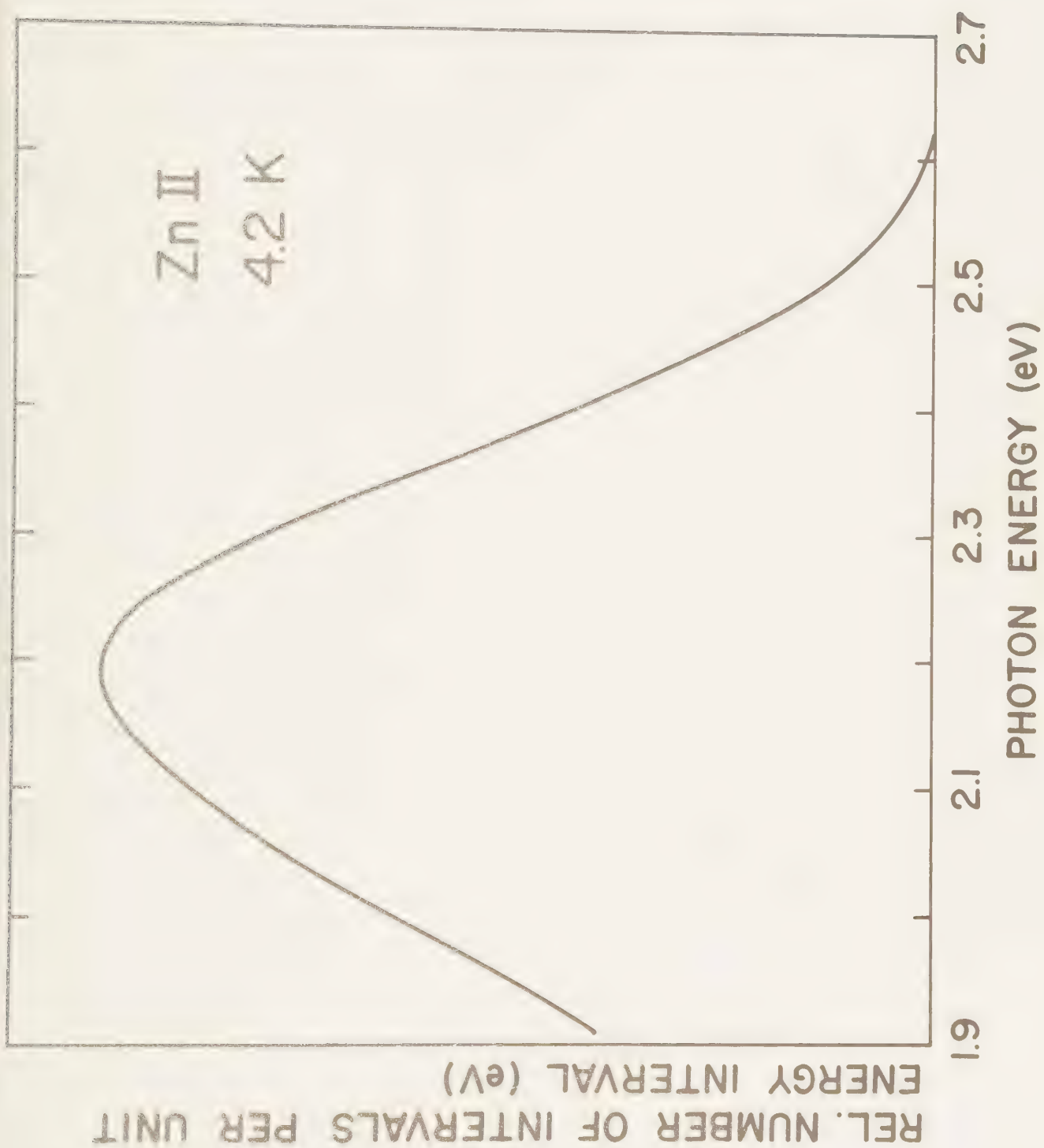


Fig. 13

REL. NUMBER OF PHOTONS PER UNIT ENERGY
INTERVAL (LINEAR SCALE)

Zn IV
293 K

1.50 1.90 2.30 2.70 3.10
PHOTON ENERGY (eV)



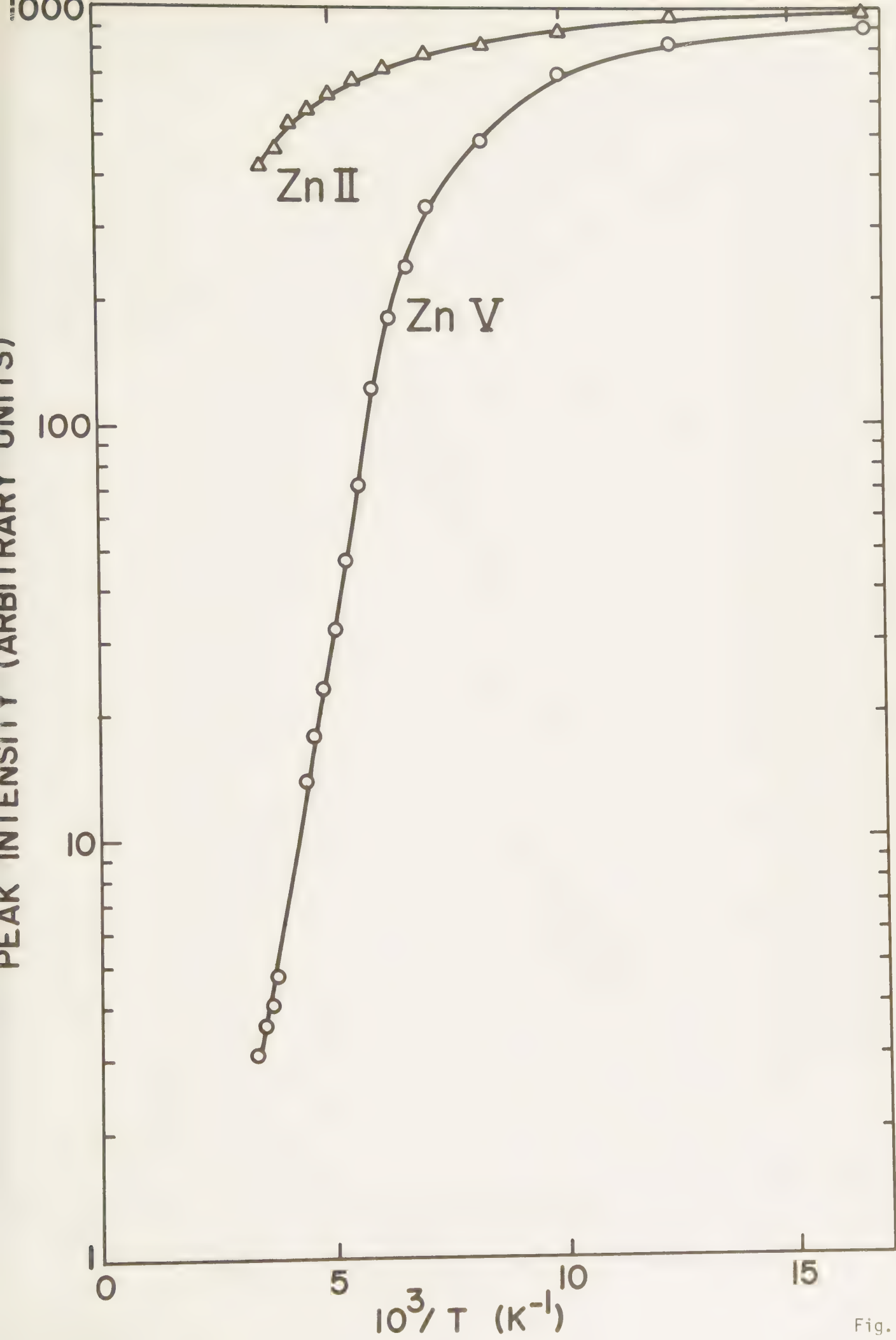


Fig. 15

REL. NUMBER OF PHOTONS PER UNIT ENERGY INTERVAL (LIN. SCALE)

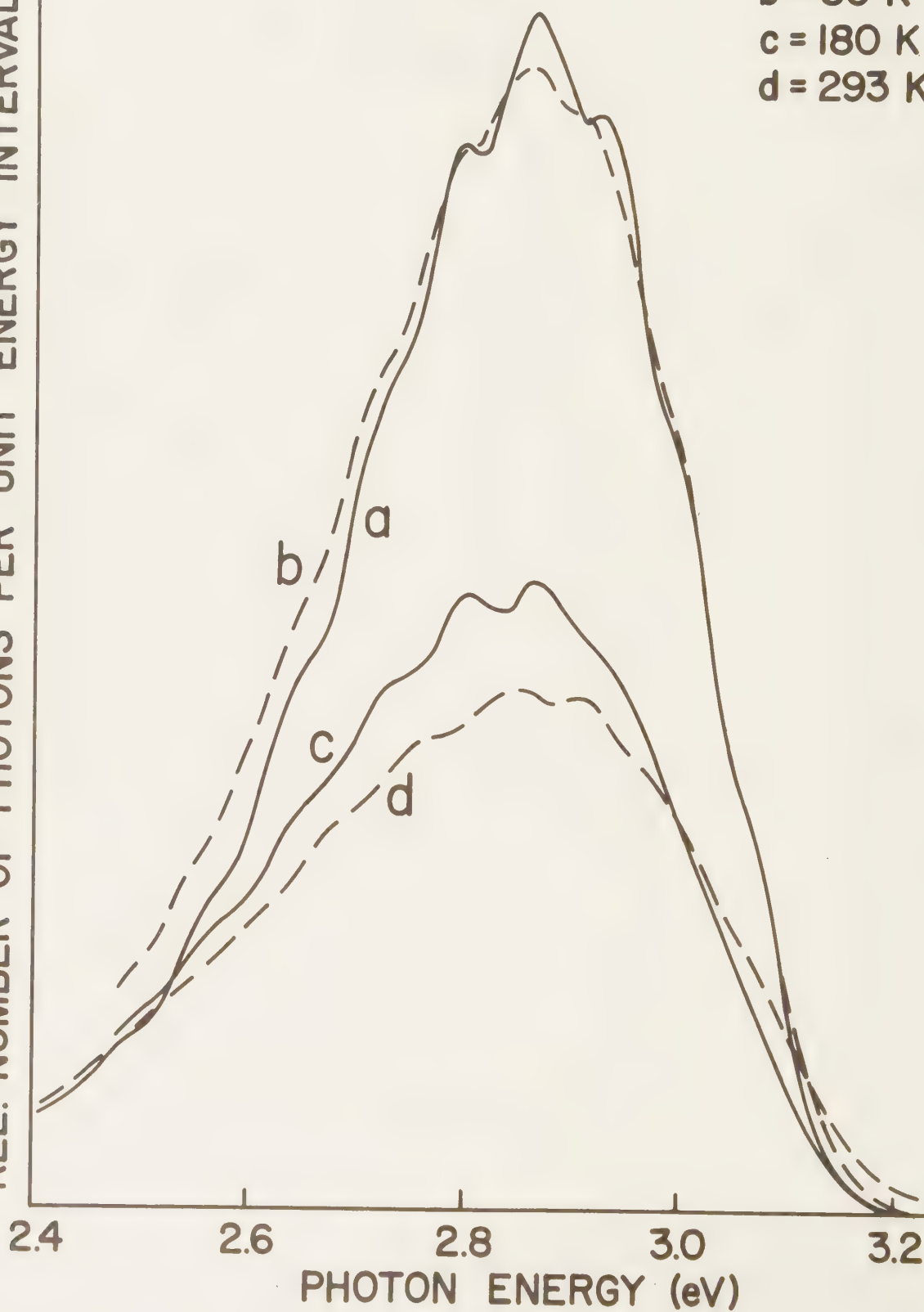
Zn I

a = 5 K

b = 80 K

c = 180 K

d = 293 K



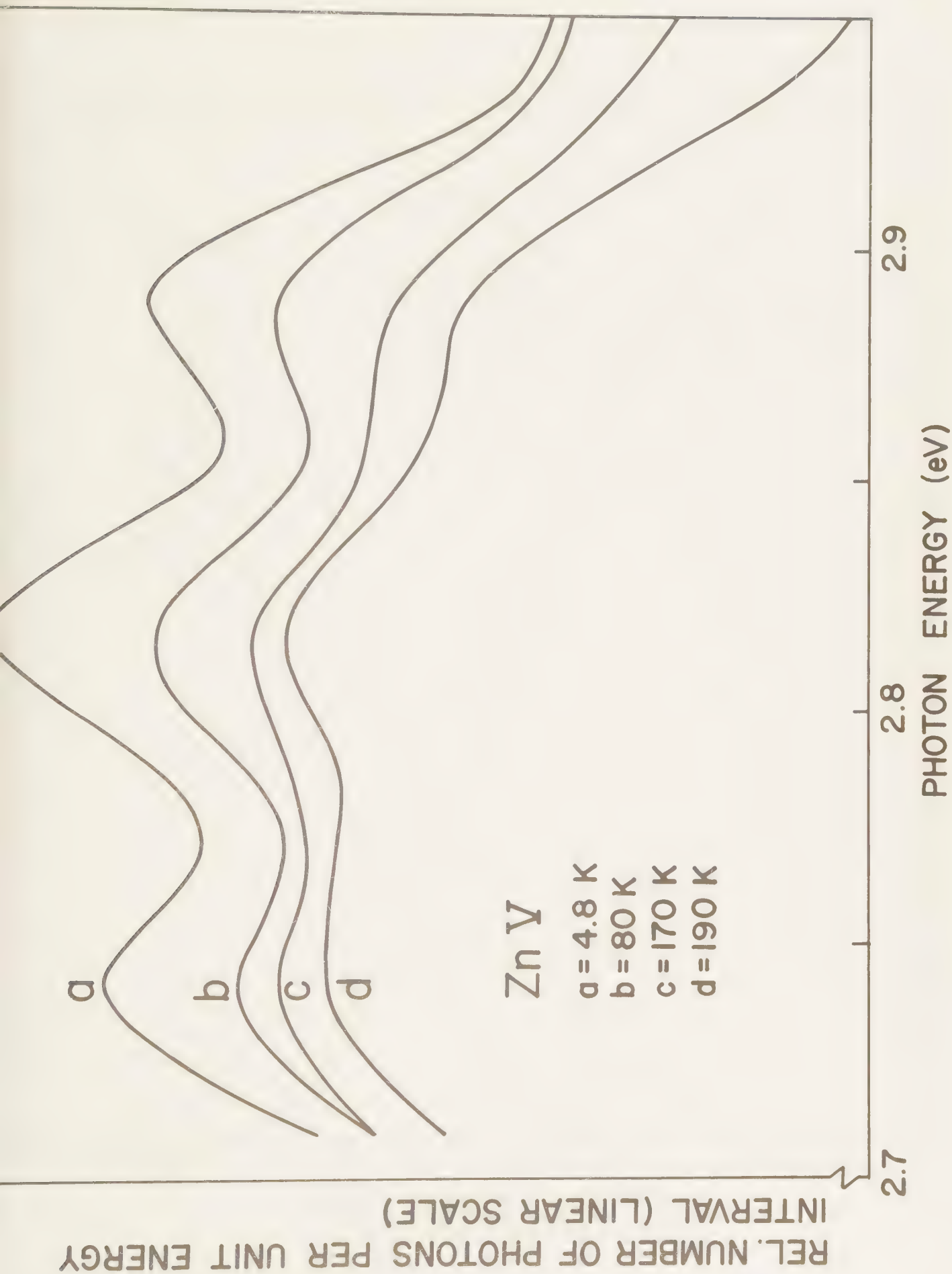
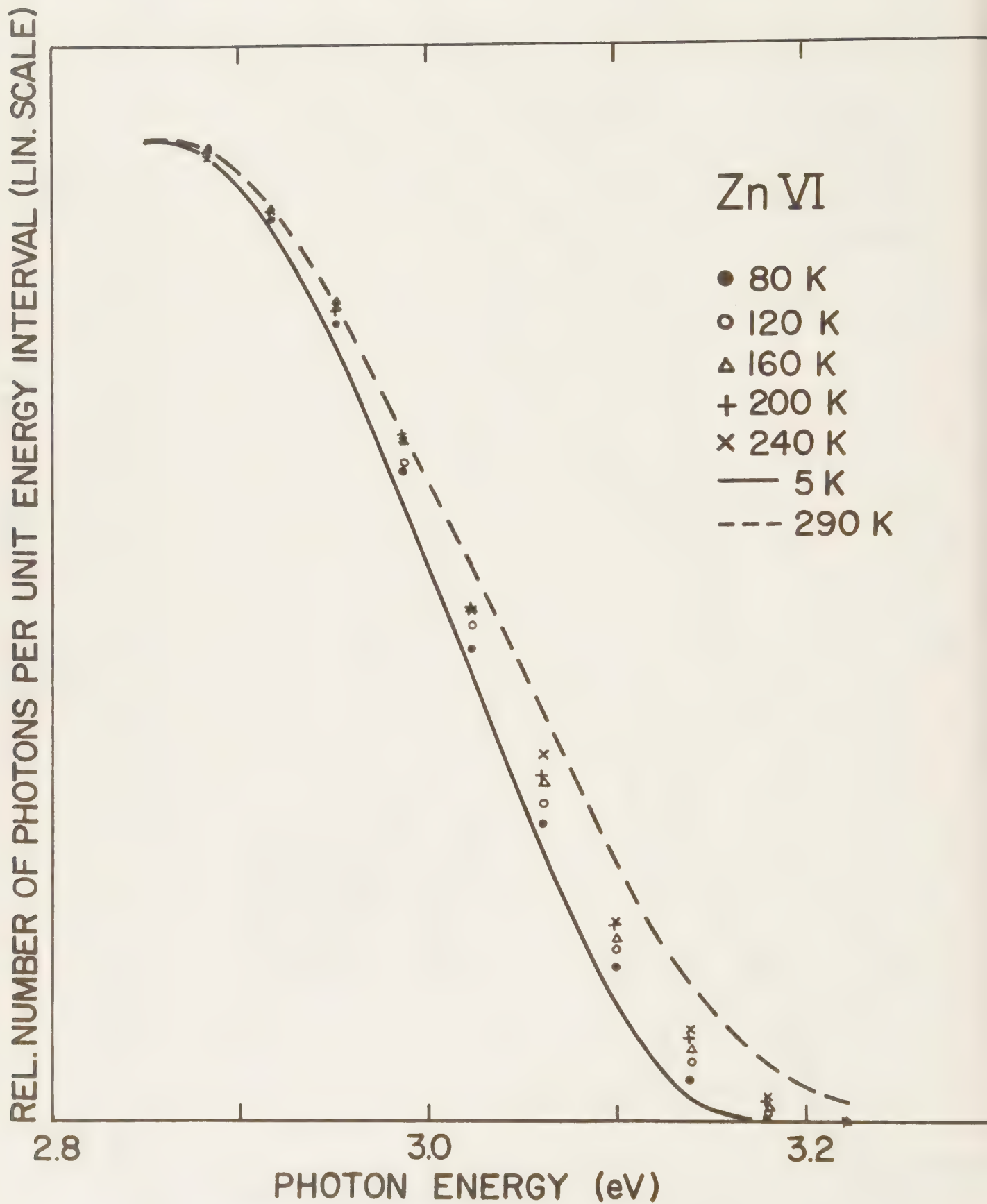


Fig. 17



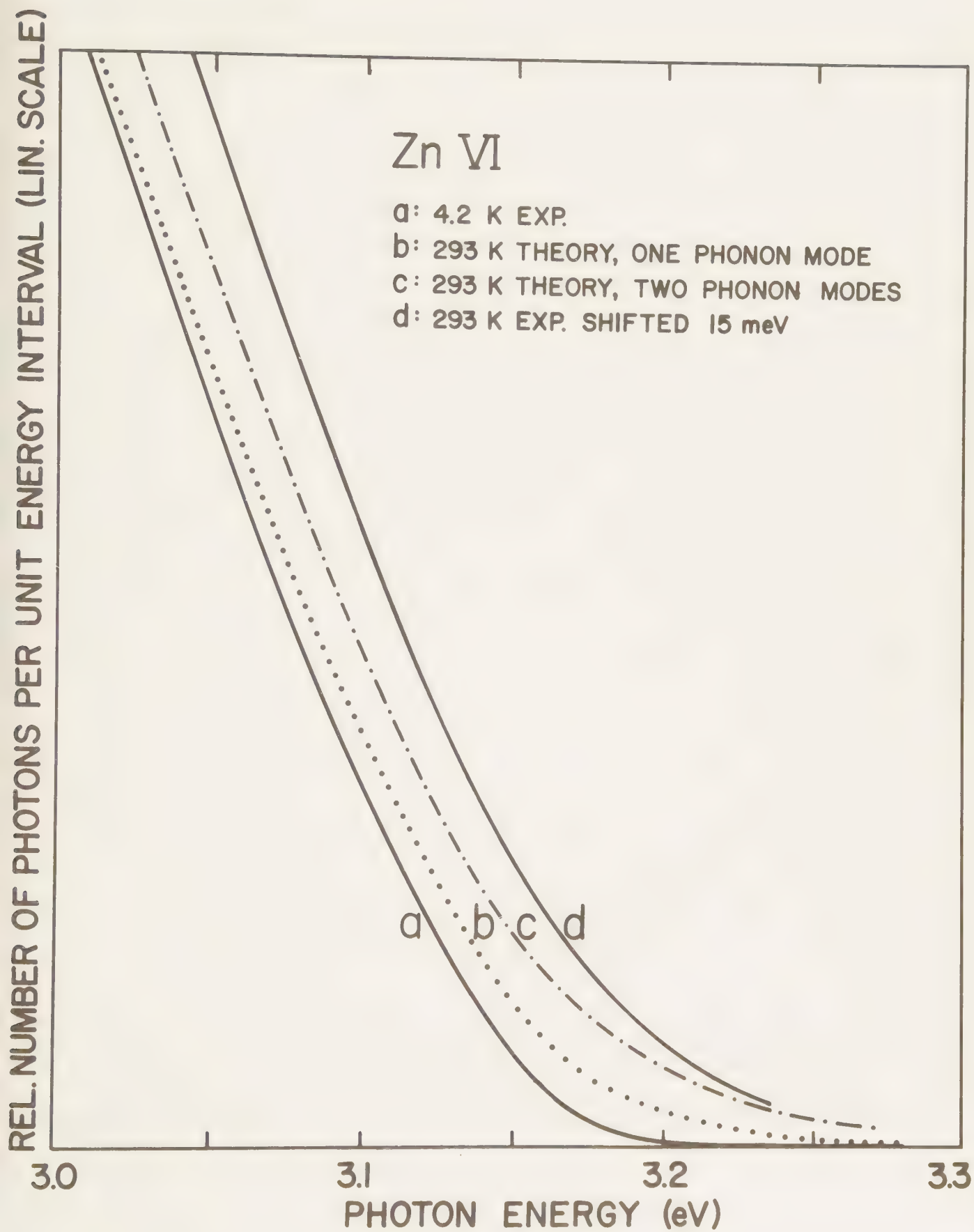
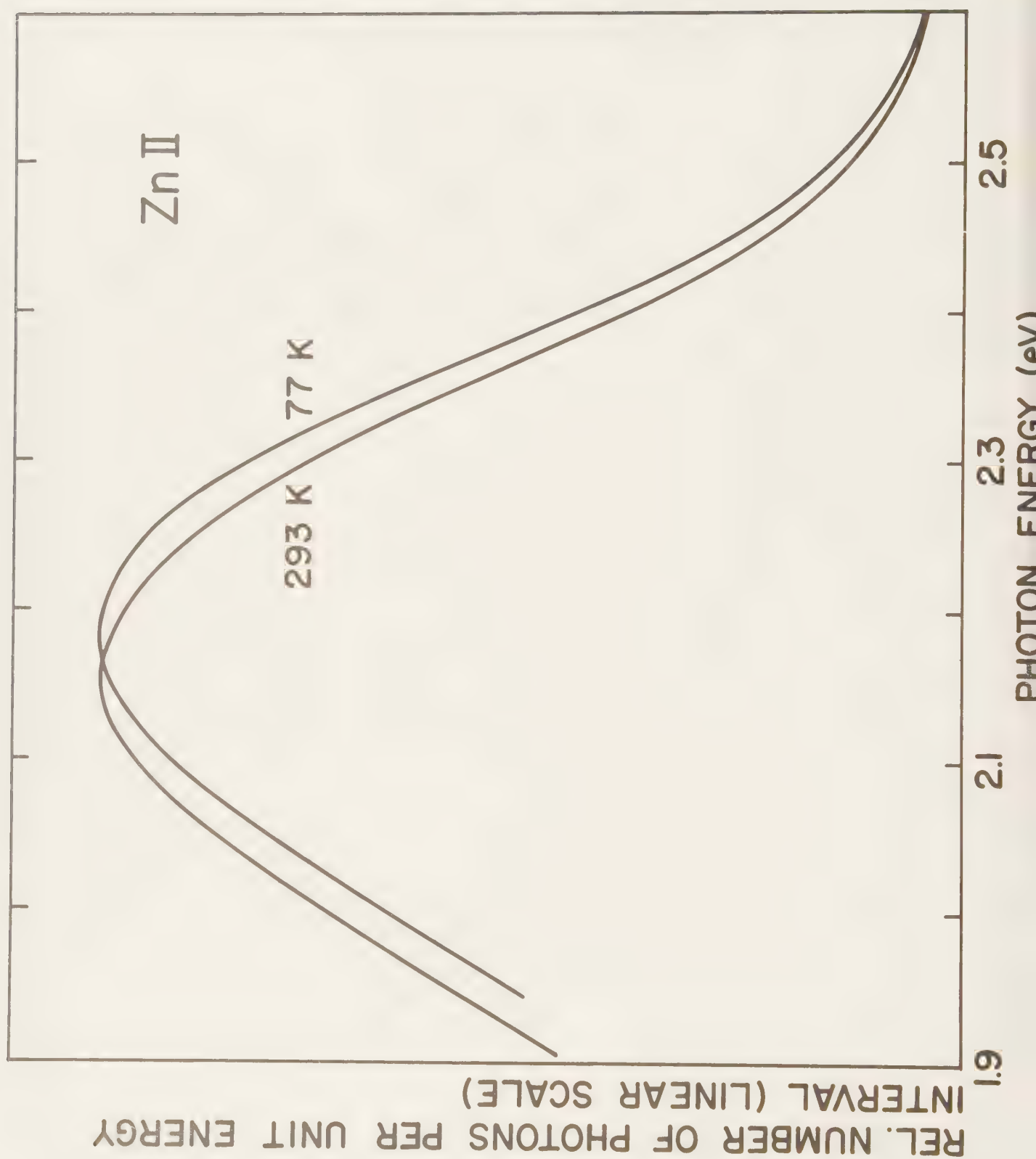


Fig. 19



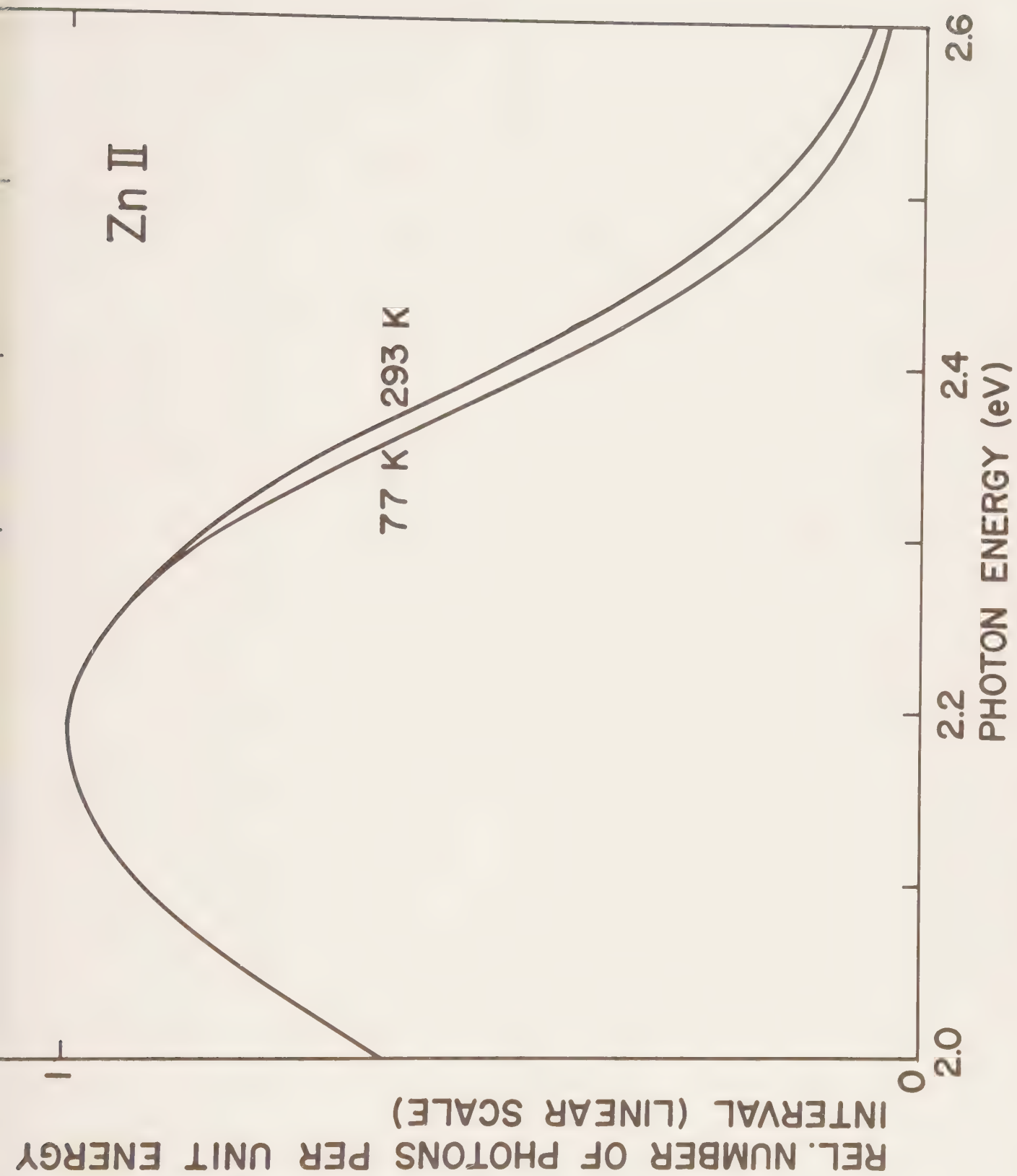


Fig. 21

Properties of Zn-doped VPE-grown GaN:

II. Optical Cross Sections

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Abstract

Experimental data are presented for optical cross sections $\sigma_n^0(h\nu)$ related to the four deep acceptorlike Zn-related radiative levels A-D in GaN. Very sensitive spectral data were obtained by the photoluminescence excitation (PLE) technique, at temperatures varying from 4.2 K up to 293 K. From a detailed comparison of the spectral behaviour of the emission and absorption spectra, the size of electronic broadening effects could be determined in the overlap region. The binding energies for Zn-related acceptor levels were obtained as $E_A = 0.34 \pm 0.04$ eV, $E_B = 0.65 \pm 0.08$ eV, $E_C = 1.02 \pm 0.05$ eV and $E_D = 1.43 \pm 0.08$ eV at low temperature. Optical transmission data give estimates of absolute values for optical cross sections at saturation, varying from $\sigma_{n_A}^0(\text{sat}) \approx 1 \cdot 10^{-16} \text{ cm}^2$ to $\sigma_{n_D}(\text{sat}) \approx 5 \cdot 10^{-18} \text{ cm}^2$. Temperature broadening effects in optical cross sections are well explained by a linear model for phonon coupling in the optical transitions, employing the same phonon energies and coupling strengths as were evaluated from emission spectra.

I:1 Introduction

Zn is one of the acceptor dopants that are readily introduced into GaN during VPE growth [1-4]. It has been shown that Zn can provide efficient radiative recombination centres in the material, as well as electrical compensation of shallow donors [4-6]. Zn-doped GaN material is therefore most promising for applications in e.g. light-emitting devices, due to the capability of covering even the blue part of the spectrum. Actually in the preceding paper [7], we have shown that different Zn-related levels in rather heavily Zn-doped GaN can provide emission colours in blue, green, yellow and red. The emission properties of these levels were described in detail [7]. In this part we report on properties of optical cross sections, i.e. optical excitations from Zn-related levels to continuum states in the conduction band (or valence band). Such properties give important information on physical parameters of the defect levels introduced by Zn, and also determine the usefulness of Zn-doped material in photoconducting applications. In the preceding paper were described photoluminescence properties of 4 different Zn-related levels in GaN: A (0.4 eV), B (0.7 eV), C (1.0 eV) and D (1.4 eV), where approximate binding energies for the levels evaluated from emission spectra are shown in parenthesis. It is assumed that these levels are acceptorlike, i.e. the denoted energy distances are those from the valence band. The main argument for this assumption is the behaviour of photoconductivity (PC) spectra in Zn-doped material, where the excitations to the conduction band are believed to be observed [4,6]. Such detailed PC spectra have only been observed for the A-level, however, and therefore conclusions about acceptor behaviour of the B-, C-, and D-levels are

essentially based on the observations of efficient compensation of the n-type material when these levels are introduced in appreciable concentration. The exact position of the levels (A-D) could not be determined from PL spectra alone [7], due to uncertainties about the radiative processes involved, and strong electronic broadening effects in addition to vibrational broadening. The combination of PL data and detailed measurements of the spectral behaviour of optical cross sections is a much better basis for an exact evaluation of level positions. In addition accurate data for the spectral behaviour of optical cross sections can serve as a guidance for evaluation of symmetry and physical origin of the electronic levels [8,9].

In Sec. II below we describe briefly the experimental methods used in these investigations on optical cross sections, i.e. photoluminescence excitation spectra (PLE) and optical transmission. For a description of material preparation, doping and material characterization by SIMS etc. we refer to the preceding paper [7].

In Sec. III PLE-data for optical cross sections $\sigma_n^0(h\nu)$ for excitation from the Zn-levels to the conduction band are presented for levels A-C. The behaviour of these spectra is followed from the lowest temperature up to room temperature. This makes an evaluation of temperature broadening possible, for comparison with theoretical predictions. Low temperature data of $\sigma_n^0(h\nu)$ give the approximate shape of the electronic cross section $\sigma_{n,el}^0(h\nu)$ for the A- and C-levels from a deconvolution procedure.

In Sec. IV transmission data for Zn-doped GaN are presented, which

allow a rough estimate of absolute values of optical cross sections $\sigma_n^0(h\nu)$ for the Zn-related levels A-D.

In Sec. V a more detailed discussion of the available data is presented. A rather accurate evaluation of the level positions for levels A-D is presented by comparison between emission and absorption spectra. This comparison for low temperature data also gives a good measure of the magnitude of electronic broadening effects. The properties of the levels are discussed in relation to the spectral behaviour of optical cross sections. Temperature broadening effects are also found to be reasonably well explained by the phonon coupling parameters determined from emission spectra, using a linear model for phonon coupling.

II. Experimental techniques

II:1 PLE-measurements

The technique of photoluminescence excitation spectra (PLE) has already proved to be a very powerful method to selectively measure the spectral behaviour of an optical cross section, being the reverse transition for the observed emission [9]. From Fig. 1 is clear, that under the conditions of our experiments, i.e. the equilibrium fermi level E_F is situated in the upper half of the bandgap, the detected intensity of the radiation emission L_T is directly proportional to the optical cross section $\sigma_{nT}(h\nu)$ at each $h\nu$, or more specifically

$$\sigma_{nT}^0(h\nu) = \frac{\beta^{-1} L_T}{N_{TT} \Phi}, \quad (1)$$

where β is the radiative efficiency of the recombination via T, and Φ is the employed excitation intensity. If L_T is linear in Φ as in Fig. 2, $\sigma_n^0(h\nu)$ is simply obtained from a scanned recording of the PLE-spectrum, linearly corrected for the employed excitation intensity $\Phi(h\nu)$. In the data to be reported here, β was not determined, and therefore only the spectral behaviour of optical cross sections $\sigma_n^0(h\nu)$ has been obtained from PLE-data. An estimate of absolute values of cross sections is attempted from transmission data. Usually it is possible in PLE-measurements to simply use a broadband optical filter in front of the detector to select out the emission to be detected. In the case of Zn-doped GaN, the presence of different, broad partially overlapping emission bands made it impossible to obtain a selective PLE-spectrum for one emission only by employing optical filters. We therefore had to use a Zeiss MM12 double prism monochromator as a filter in front of the detector, to select a suitably narrow spectral region for detection, and to avoid straylight from the excitation to enter the detector. The set-up used is schematically shown in Fig. 3.

II:2 Optical transmission measurements

The spectral dependence of the optical absorption coefficient $\alpha(h\nu)$, as obtained directly from an optical transmission experiment, gives direct information on the magnitude of optical excitation processes via localized levels in the bandgap. The magnitude of α at each photon energy can thus be expressed as

$$\alpha = \sum_{i=1}^N N_{Ti} \cdot \sigma_{n_{Ti}}^0(h\nu), \quad (2)$$

where N is the concentration of levels labelled i , and $\sigma_{Ti}^0(h\nu)$ is the

corresponding optical cross section for excitation via these levels to the conduction band. In (2) we have further assumed that all levels are completely filled in thermal equilibrium, thus neglecting contributions from excitations from the valence band (Fig. 4). If the concentrations of different levels are known, this procedure allows an absolute measurement of the different cross sections $\sigma_{n_{Ti}}(h\nu)$, assuming they can be separated spectrally by some method.

III. PLE-data on optical cross sections for Zn-related levels A - C

III:1 Spectral dependence of cross sections from low temperature data

The PLE-method of measuring the spectral behaviour of optical cross sections is very sensitive in the visible and near ir region of the spectrum (due to the availability of sensitive photomultipliers). As already mentioned, it is also a method of measuring optical cross sections selectively (i.e. contributions from optical excitations via other centres are not measured simultaneously), provided the PL-emission characteristic for the centre under study can be sufficiently well isolated. This point is illustrated in Fig. 5, where PLE-spectra are shown for a crystal which gives comparable intensities for all Zn-related emissions A-D, when above bandgap (or near bandgap) excitation is employed. For detection at $h\nu \approx 2.88$ eV or above we observe only the $\sigma_{n_A}^0(h\nu)$ cross section, while for detection at lower photon energies, cross sections $\sigma_{n_B}^0(h\nu)$ and $\sigma_{n_C}^0(h\nu)$ also contribute (Fig. 5). In the following we shall show data for cross sections $\sigma_{n_A}^0(h\nu)$, $\sigma_{n_B}^0(h\nu)$ and $\sigma_{n_C}^0(h\nu)$, measured in suitable crystals and at detection wavelengths optimized for a selective measurement. Unfortunately reliable data for

$\sigma_{n_D}^0(h\nu)$ could not be obtained, since in this case strong excitations of red emissions in the sapphire windows of the cryostat interfered seriously with the measurements.

The optical cross section $\sigma_{n_A}^0(h\nu)$, measured at 4.2 K with PLE-technique, is shown in Fig. 6. It is noted that in spite of the unfavourable detection arrangement with a narrow slit double monochromator as filter (Fig. 3), nearly five orders of magnitude of the threshold region between 3.0 and 3.3 eV could be measured. A monotonic rise of the curve is observed, with a tendency for saturation above 3.4 eV. It is further noted that at energies above the bandgap, only a small rise in the PLE-spectrum is observed at these high doping levels ($10^{19} - 10^{20} \text{ cm}^{-3}$), which means that capture processes involving carriers excited directly across the bandgap are not dominating. This is different from the case of lower doping ($\ll 10^{19} \text{ cm}^{-3}$), where a marked rise in the PLE-spectrum close to the bandgap is observed [10].

In Fig. 6 is also included an "electronic" spectrum $\sigma_{n_A,el}^0(h\nu)$, obtained by deconvolution [9] of the experimental curve $\sigma_{n_A}^0(h\nu)$ with the assumption of a linear coupling model and the same fundamental phonon energy (74 meV) and coupling strength ($\lambda = 3$) as was obtained from the detailed studies of the A-emission in the preceding paper [7]. The so obtained electronic curve shows a peak already at about 3.25 eV, i.e. rather close to the threshold. Indeed a peak position in $\sigma_{n_A,el}^0(h\nu)$ close to the threshold is expected for a parity-allowed transition from an acceptor-like state to the conduction band, if one assumes a localized (δ -function) potential for the deep state [9,11]. A detailed analysis of the shape of the obtained $\sigma_{n_A,el}^0(h\nu)$ -curve may not be warranted from

the present data, however. One reason for that is a possible slight distortion of the PLE-spectrum above about 3.3 eV due to the high absorption coefficient (see below Sec. III:2). At higher photon energies the excited carrier profile in the sample is shifted towards the surface. As long as the emission intensity is linear with excitation intensity this effect can only influence our measured PLE-curve when the influence of surface recombination is changed with $h\nu$.

Since we estimate excess carrier diffusion lengths to be $< 1 \mu\text{m}$ in highly doped GaN material, such effects could only cause very small distortions in our case. Another problem is the drastic broadening behaviour observed down in the edge region below 3.1 eV, even at the lowest temperatures. This effect will be discussed further below in Sec. V, where an evaluation of the "unperturbed" threshold energy for the A-level is also attempted.

For the B-level the corresponding $\sigma_{nB}^0(h\nu)$ optical cross section turned out to be extremely difficult to measure. The reason for this was that at our growth temperature (1025 - 1050 °C) the corresponding B-emission peaking at about 2.6 eV [7] was always weaker than A- and C-emissions at any choice of Zn-concentration. Therefore $\sigma_{nB}^0(h\nu)$ could not be measured separately from the $\sigma_{nA}^0(h\nu)$ or $\sigma_{nC}^0(h\nu)$ cross sections with any degree of sensitivity comparable to those. However, as shown in Fig. 7, a contribution from $\sigma_{nB}^0(h\nu)$ can clearly be observed in PLE-spectra from some crystals. The limited range of observation of $\sigma_{nB}^0(h\nu)$ only permit the conclusion that the edge of this cross section is close to 2.8 eV at 293 K. Comparison with the B-emission threshold shows that this is consistent with the observed position of the edge of the luminescence spectrum associated with the B-level [7].

The $\sigma_{nC}^0(h\nu)$ optical cross section could again be measured rather conveniently by the PLE-technique, since the corresponding C-emission was fairly strong in some samples and well separated from the blue A-emission. In Fig. 8 is shown the low temperature behaviour of $\sigma_{nC}^0(h\nu)$, measured in PLE with the detection system set at $h\nu \approx 2.14$ eV. Under these conditions, about 3 orders of magnitude of the edge of $\sigma_{nC}^0(h\nu)$ could be measured at 4.2 K, the lower limit set by the background caused by a small contribution of excitation transfer from other centres. The edge of $\sigma_{nC}^0(h\nu)$ occurs at about 2.25 eV at 4.2 K. As is evident from the appearance of the luminescence spectrum [7], a substantial electronic broadening effect is present also for the C-level, which affects the detailed evaluation of the unperturbed edge (see below Sec. V). A deconvolution of the obtained $\sigma_{nC}^0(h\nu)$ spectrum was also performed, assuming linear phonon coupling with the same one-phonon parameters as obtained from an analysis of the C-emission [7], i.e. $\hbar\omega = 84$ meV, $\lambda = 3$. The resulting $\sigma_{nC,el}^0(h\nu)$ curve shows a peak at about 2.58 eV, i.e. rather close to the unperturbed threshold (see below Sec. V). This behaviour is quite similar to what was found above for the $\sigma_{nA,el}^0(h\nu)$ cross section.

III:2 Temperature broadening of optical cross sections

The optical cross section $\sigma_{nA}^0(h\nu)$ and $\sigma_{nC}^0(h\nu)$ could be measured at all temperatures below 293 K with good sensitivity using the above mentioned PLE-technique. Since the $\sigma_{nB}^0(h\nu)$ could just barely be observed, data for comparison of behaviour at different temperatures would not be meaningful for this cross section. Further, as already mentioned, the

D-level cross section $\sigma_{n_D}^O(h\nu)$ could not be measured accurately at any temperature, due to the strong appearance of red emissions from the sapphire windows with excitation around 2.1 - 2.2 eV at all temperatures.

In Fig. 9 are shown experimental $\sigma_{n_A}^O(h\nu)$ cross sections obtained from PLE-data at different temperatures between 4.2 K and 290 K. The curves have been normalized to the same value at 3.35 eV, since above this energy spectral broadening is neither expected nor observed. Effects of broadening with rising temperature are expected from the lattice relaxation effects observed in PL-emission spectra for the A-centre [7], and indeed the presence of such effects is evident from Fig. 9. In an evaluation of the magnitude of this broadening for a comparison with theoretically predicted broadening effects, the rigid shift of the cross section towards lower energy, due to the corresponding shift of the electronic A-level with temperature has to be considered. Such a comparison of experimental curves with theoretical curves, obtained by a convolution procedure [9,12] employing the low temperature electronic cross section (Fig. 6) and phonon coupling parameters the same as in the A-emission [7] (i.e. $\hbar\omega = 74$ meV and $\lambda = 3$) was undertaken, as shown in Fig. 10. It seems evident that the experimental broadening effects are substantially larger than expected from the simple linear theoretical model for CC-phonon coupling, if only the fundamental 74 meV mode is included. The broadening of the theoretical curve due to the single 74 meV phonon (curve d in Fig. 10) is only about half the experimental broadening, as obtained from curve b, which is identical with the a-curve shifted 15 meV to higher energy to account for the level shift in the bandgap with temperature [7]. From

a similar analysis of photoluminescence spectra in the preceding paper [7], it was concluded that a second unresolved lower energy mode was also active in the optical transitions to the A-centre. If we include this second phonon mode in the theoretical calculation of spectral broadening, additional broadening is indeed produced. Curve c of Fig. 10 shows the calculated convoluted $\sigma_{nA}^0(h\nu)$ curve at 293 K, employing the same total phonon coupling parameters $\hbar\omega_{A1} = 74$ meV, $\lambda_{A1} = 2.8$, and $\hbar\omega_{A2} = 20$ meV, $\lambda_{A2} = 2$ as for the A-emission [7]. The discrepancy between experimental and theoretical broadening is then reduced to about 25 %. We think this agreement confirms that the temperature broadening effects observed are, as expected, dominated by the lattice relaxation phenomena in optical transitions. In the presence of very strong electronic broadening effects on $\sigma_{nA}^0(h\nu)$ (see below Sec. V) a better agreement might not be expected.

Similar experimental data for the $\sigma_{nC}^0(h\nu)$ cross section could also be obtained by PLE measurements between 4.2 K and 293 K, as shown in Fig. 11 for two different temperatures, 4.2 K and 293 K. It was observed that the 4.2 K and 77 K curves are almost identical, while the 293 K curve is shifted towards lower energy, and also somewhat broadened. The theoretically expected behaviour of the 293 K curve, obtained from a convolution procedure [9,12] of the electronic $\sigma_{nC,el}^0(h\nu)$ curve in Fig. 8 is also included in Fig. 11 (curve c). A comparison of this one-mode theoretical curve (curve c) with the experimental 293 K (curve b), shifted 30 meV to higher energies to account for the approximate shift of the C-level in the bandgap with temperature, reveals a discrepancy of about a factor 2 in broadening, similar to the case of the $\sigma_{nA}^0(h\nu)$ cross section (Fig. 10). Including

a second phonon mode as for the A-level would similarly improve the agreement between experimental and theoretical broadening of $\sigma_{nC}^0(h\nu)$. An even larger electronic broadening for the C-level (see below Sec. V), together with somewhat more uncertain experimental data compared to the A-level, made such a detailed analysis unwarranted.

IV. Optical absorption data

Selected areas on some of the Zn-doped crystals were sufficiently smooth to allow optical transmission measurements on the layers. These measurements were performed on the as-grown layers, retaining the 250 μm thick sapphire substrate. The transmission data were analysed according to the simple formula

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (3)$$

where α is the absorption coefficient, d is the GaN layer thickness (50 - 100 μm), R is an effective reflexion factor (also taking into account reflexion losses in the sapphire substrate), and T the measured transmission. An example of the resulting spectral dependence for the absorption coefficient $\alpha(h\nu)$, measured at 77 K, is shown in Fig. 12. The curve shows only a very slow rise in α in the region 2.0 - 3.0 eV, indicating this region is the saturation region for optical cross sections associated with deep levels with threshold energies below 2.0 eV. Above 3.0 eV the curve rises more sharply, and values for α above 3.2 eV could not be obtained with the crystal thicknesses available for Zn-doped material. We interpret this rise above 3.0 eV as the onset of the $\sigma_{nA}^0(h\nu)$ cross section. Equating that at 3.2 eV about $5 \cdot 10^2 \text{ cm}^{-1}$ of the total value of α comes from the $\sigma_{nA}^0(h\nu)$ cross

section, and assuming that of the total Zn-concentration of about $8 \cdot 10^{19} \text{ cm}^{-3}$ [7] the A-centres contribute a share of $2 \cdot 10^{19} \text{ cm}^{-3}$, we obtain an absolute value of $\sigma_{n_A}^0(h\nu)$ as $2.5 \cdot 10^{-17} \text{ cm}^{-2}$ at 3.2 eV. This corresponds to a value around $2 \cdot 10^{-16} \text{ cm}^{-2}$ in the saturation region above 3.4 eV (Fig. 6). Considering the uncertainties involved, particularly in the determination of the concentration of A-centres, it can only be appropriate at this stage to suggest a saturation value $\sigma_{n_A}^0(\text{sat}) \approx 10^{-16} \text{ cm}^{-2}$ above 3.4 eV, with an uncertainty that could be as large as an order of magnitude.

Assuming the observed absorption below 3.2 eV is also partly due to the Zn-related levels B-D, a similar estimate can be done of the order of magnitude of corresponding optical cross sections. In Fig. 12 it is possible to observe a rise at approximately the expected positions for $\sigma_{n_B} - \sigma_{n_D}$, which supports this assumption. If this is correct, and if the concentration of levels B, C, and D in this sample is similar to the A-concentration, approximate saturation values for optical cross sections are obtained as $\sigma_{n_B}^0(\text{sat}) \approx 3 \cdot 10^{-17} \text{ cm}^{-2}$, $\sigma_{n_C}^0(\text{sat}) \approx 5 \cdot 10^{-18} \text{ cm}^{-2}$, and $\sigma_{n_D}^0(\text{sat}) \approx 5 \cdot 10^{-18} \text{ cm}^{-2}$. The sample used showed all four emissions A-D at comparable intensities. The above assumption of approximately equal concentrations for these levels A-D may of course not be warranted from this observation alone, which motivates an uncertainty for the obtained saturation values for optical cross sections of at least an order of magnitude. The values obtained are in the range usually observed for optical cross sections [13], supporting the assumption that the measured PLE quantities are actually optical cross sections. (This point will be further discussed below.)

V. Discussion

V:1 Comparison between emission and absorption data for the same levels

In the preceding paper a detailed investigation on radiative emission properties for Zn-related levels A-D in GaN was presented. One of the properties noted for all these emission was a rather strong broadening effect on the electronic part of the transitions, which made any evaluation of the exact position of the energy levels associated with these four emissions very uncertain. It was noted e.g. that the high energy tail of the blue A-emission could be detected up to 3.20 eV, even at the very lowest temperatures, while the electronic peak was situated at about 3.10 eV [7]. An estimate of the size of such broadening effects can be obtained if the radiative emission spectrum, shown as $\frac{I(\nu)}{\nu^3}$ (see below), and the corresponding modified absorption cross section (or $\frac{\sigma(\nu)}{\nu}$, see below) are plotted together in the same figure, as shown in Fig. 13 for the A-level, using data obtained at 4.2 K. When the curves are normalized to the same maximum height, a considerable overlap region is observed. The cross-over point in this curve is observed at around 3.16 eV at 4.2 K. If no electronic broadening was present, one would expect both spectra to come to zero at this position, under the simple assumption of a free-to-bound transition for the A-emission. Knowing the value of the bandgap as 3.50 eV at this temperature [14], it is possible to ascribe a value $E_A \approx 3.50 - 3.16 = 0.34$ eV to the A-level binding energy.

In Fig. 13 is also shown a fictitious absorption curve (curve c), which shows the expected spectral behaviour of the excitation spectrum in the case of an internal transition within a centre. This is obtained from

the general expressions for the absorption and emission probabilities for the same electronic transitions, obeying the relations $\sigma(\nu) \propto |M|^2 \cdot \nu$ (absorption) and $I(\nu) \propto |M|^2 \cdot \nu^3$ (emission) [15]. Here M denotes the optical matrix element and $h\nu$ the photon energy. From these relations it is evident, that a mirror image of $\frac{I(\nu)}{\nu^3}$ should coincide with the curve $\frac{\sigma(\nu)}{\nu}$, if the hypothesis of an internal transition was correct. If on the other hand the $\sigma(\nu)$ -curve is an optical cross section, i.e. due to excitations to empty continuum states, no mirror symmetry is to be expected (due to the lack of symmetry in occupation of continuum states between emission and absorption). From the observed difference between the mirrored emission curve $\frac{I(\nu)}{\nu^3}$ and the experimental absorption curve $\frac{\sigma(\nu)}{\nu}$ shown in Fig. 13 one can conclude that the observed excitation spectrum is indeed an optical cross section. This was tacitly assumed in Sec. III above, where experimental PLE-data were described. In other words, these curves in Fig. 13 show that the A-emission is not likely to be an internal transition within a centre.

The estimate of the A-centre binding energy from the point of overlap between the curves $\frac{I(\nu)}{\nu^3}$ and $\frac{\sigma(\nu)}{\nu}$ is theoretically sound, but the assumption of a simple free-to-bound transition also in emission adds some uncertainty to the value E_A obtained from this procedure. If a donor band tail contributes significantly to the emission spectrum, the cross-over point energy is a lower bound for the estimate of $E_g - E_a$. On the other hand we do not know for certain that the electronic broadening effects give exactly the same spectral broadening in both emission and absorption. We therefore feel the estimate of E_A should be stated conservatively as $E_A = 0.34 \pm 0.04$ eV from these data. This compares favourably with the value $E_A = 0.37 \pm 0.04$ eV evaluated in the previous

paper from the behaviour of the electronic peak of the A-emission [7].

In Fig 14 are shown similar 4.2 K curves for the C-level. It is evident that the overlap region is here even more pronounced than for the A-centre. While overlap at 3.16 eV between emission $\left(\frac{I(\nu)}{\nu^3}\right)$ and absorption $\left(\frac{\sigma(\nu)}{\nu}\right)$ curves is about 2.5 % of the peak of the curve for the A-centre (Fig. 13), the corresponding strength of overlap at 2.48 eV for the C-emission is more than 10 %, indicating a very strong broadening effect (as was already noted in the previous paper). Actually it can be noted from Fig. 13 of Ref. 7 that the tail of the emission curve can be followed up to about 2.6 eV at 4.2 K, while at this same temperature the tail of the absorption curve can be observed well below 2.3 eV (Fig. 8 above). The cross-over point between the two curves should represent a fair estimate of the electronic threshold energy for unperturbed material (i.e. if broadening was absent). Accordingly we estimate the binding energy of the C-level as $E_C = 3.50 - 2.48 = 1.02 \pm 0.05$ eV at 4.2 K, where the uncertainty allows for ignorance of the details in the radiative recombination process for the C-level. For the C-level we have also made the comparison between a modified mirrored emission curve $\frac{I(\nu)}{\nu^3}$ and the modified experimental absorption curve $\frac{\sigma(\nu)}{\nu}$ to check whether the measured PLE curves are actually optical cross sections for transitions from the level to the conduction band continuum. The marked difference observed between the shape of $\frac{I(\nu)}{\nu^3}$ (curve c) and $\frac{\sigma(\nu)}{\nu}$ (curve b) shows that our designation of the PLE-curves as optical cross sections is correct for the C-level as well. Fig. 14 is therefore a strong argument against an interpretation of the C-emission as an internal transition within a centre.

Unfortunately similar comparisons between absorption and emission curves for the same level could not be obtained for the B- and D-levels since the measurements of optical cross sections were there less accurate. From a rough comparison of the emission spectrum from Fig. 12 of Ref. 7 and the absorption cross section (Fig. 7 above) we estimate an unperturbed electronic threshold at about 2.85 eV for the B-level, which means a binding energy $E_B = 3.50 - 2.85 = 0.65 \pm 0.08$ eV at 4.2 K. For the D-level we can only use the emission data of Fig. 14 in Ref. 7, and assuming a similar broadening as for the C-emission we arrive at an estimated threshold value around 2.02 eV at 293 K, which means a binding energy of $E_D = 3.45 - 2.02 = 1.43 \pm 0.08$ eV for the D-level.

We note that the knowledge of the amount of electronic broadening present in the emission curves could not be easily estimated from the emission curves alone, and therefore a reliable evaluation of the electronic level positions was not attempted in the preceding paper describing Zn-related emission properties [7].

In previous works by other authors mostly values for the A-centre binding energy have been reported. These estimates vary between 0.3 and 0.7 eV for the A-centre, depending on the various models used for the emission [1,4,6,10,16]. It is interesting to compare the experimental results on photoluminescence quenching spectra (PLQ) obtained for the A-emission in Ref. 10. (Since this measurement technique is considerably less sensitive than the PLE-technique, we did not attempt complementary PLQ-measurements of cross sections $\sigma_{PA}^0 - \sigma_{PD}^0$ in this work.) The measured quantity for the A-centre by PLQ in Ref. 10 should correspond to $\sigma_{PA}^0(h\nu)$, and from our detailed evaluation of emission and

absorption for the A-centre we should predict a threshold value around 0.34 eV for $\sigma_{PA}^0(h\nu)$. On the contrary, a value of 0.48 eV was evaluated in Ref. 10 from a fit of the PLQ-curve to a theoretical expression [17]. However, less than an order of magnitude of the rise of the $\sigma_{PA}^0(h\nu)$ -curve was obtained in these PLQ-data. We predict that a more sensitive measurement would have revealed a region of the $\sigma_{PA}^0(h\nu)$ edge extended towards lower photon energies. Therefore we do not consider these PLQ-data as inconsistent with our interpretation of the binding energy of the A-level as $E_A = 0.34 \pm 0.04$ eV. In another set of data on photoconductivity of Zn-doped GaN a low temperature edge related to excitations in the $\sigma_{nA}^0(h\nu)$ cross section was observed at about 3.12 eV at 77 K [4], consistent with our evaluated value of the binding energy E_A .

For the emissions B-D only preliminary data from one other group is available to compare the evaluated data for binding energies. Boulou et al. [18] report binding energies $E_A = 0.33 \pm 0.07$ eV, $E_B = 0.8 \pm 0.1$ eV, and $E_C > 1$ eV from their evaluation of PL emission properties alone. We note a good agreement for the A-centre, while our value for E_B is smaller than theirs (although the estimated ranges of uncertainty do overlap in the two cases).

V:2 Temperature broadening effects

The most obvious reason for observing broadening effects with temperature in optical cross sections for deep impurities in semiconductors is the lattice relaxation, i.e. interaction with configuration coordinate (CC) phonons upon optical transitions (Fig. 15). The broadening is then

imagined as due to the "anti-stokes" components in the phonon line shape function [19,20], i.e. phonon replica of the electronic cross section appear at photon energies lower than the electronic threshold. The amplitude of these anti-Stokes replica is strongly temperature dependent, approximately reflecting the thermal occupation (Bose-Einstein distribution) of excited vibrational levels in the initial state of the optical transition. The analysis made above in Sec. III:2 of experimental data for temperature broadening of Zn-related optical cross sections $\sigma_{n_A}^0(h\nu)$ and $\sigma_{n_C}^0(h\nu)$ shows that the assumption of a linear model for the electron-phonon interaction with two phonon modes, adopted from the analysis of radiative emission data for levels A and C [7], well explains the experimental data obtained in this paper, when proper account has been taken to the independently evaluated shift of the discrete levels within the bandgap. If a substantial nonlinear contribution had been present in the phonon coupling, such good agreement between emission and absorption would not be expected. We note that a similar good success of a linear model for the phonon coupling was obtained for the deep O-donor in GaP, where data were not much affected by electronic broadening effects [9,12].

VI. Conclusions

Experimental data are presented for the spectral behaviour of optical cross sections $\sigma_n^0(h\nu)$ for several Zn-related acceptorlike levels in GaN. With the aid of photoluminescence excitation spectra about five orders of magnitude could be observed of the edge region of $\sigma_{n_A}^0(h\nu)$ for the A-level, and about three orders of magnitude of $\sigma_{n_C}^0(h\nu)$ for

the C-level. As in the case of luminescence spectra for these levels, the spectral shape of optical cross sections is dominated by a phonon envelope, due to moderately strong phonon coupling in the optical transitions. The behaviour of the electronic part $\sigma_{n,el}^0(h\nu)$ for levels A and C indicate allowed optical matrix elements as might be expected for acceptor-conduction band transitions. No accurate spectral data could be measured for the B-level, due to difficulties to isolate the B-emission from the A-emission. A similar problem occurred for the deeper D-level.

Absolute magnitudes of these optical cross sections $\sigma_n^0(h\nu)$ for levels A-D at their saturation points, could be estimated from optical transmission data. The obtained saturation magnitudes $\sigma_n^0(\text{sat})$ vary from about $1 \cdot 10^{-16} \text{ cm}^2$ for the A-level to about $5 \cdot 10^{-18} \text{ cm}^2$ for the D-level with an uncertainty that could be as much as an order of magnitude.

A comparison was made between emission and absorption spectra for levels A, B, and C, as an attempt to accurately evaluate the level positions in the bandgap. Assuming all four levels are acceptors in the lower part of the bandgap, we deduce binding energies to the valence band as $E_A = 0.34 \pm 0.04 \text{ eV}$, $E_B = 0.65 \pm 0.08 \text{ eV}$, $E_C = 1.02 \pm 0.05 \text{ eV}$ and $E_D = 1.43 \pm 0.08 \text{ eV}$ at low temperatures. Very large electronic broadening effects were revealed by this comparison, in particular for the C-centre. This broadening behaviour is believed to be mainly induced by the high doping level in these samples ($> 10^{19} \text{ cm}^{-3}$). From a comparison of the mirrored optical matrix element for emission $\frac{I(\nu)}{\nu^3}$ with the matrix element in absorption $\frac{\sigma(\nu)}{\nu}$ it was further

concluded that the measured $\sigma_n^0(h\nu)$ spectra were indeed optical cross sections for bound-to-free carrier excitations, which means that at least emissions A and C are not likely to be built up by internal transitions within centres.

The temperature induced broadening of optical cross sections $\sigma_{nA}^0(h\nu)$ and $\sigma_{nC}^0(h\nu)$ could also be accurately studied from PLE-data in this work. The theoretically expected broadening, obtained from a convolution of the electronic lineshape (which in turn was obtained from a deconvolution procedure of the 4.2 K data for these optical cross sections) agrees within 25 % with the experimental broadening. This is satisfactory regarding the strong electronic broadening effects that are also present in the optical spectra. The same phonon energies and coupling strengths as were found in the PL emission studies were used in the calculation of the theoretical broadening of cross sections. Therefore, an important conclusion from the comparison of results on temperature broadening effects in luminescence [7] and in optical cross sections is that a simple linear model of phonon coupling is successful in explaining lattice relaxation phenomena for these deep Zn-related levels in GaN. A similar conclusion was previously drawn from more accurate data on the deep 0-centre in GaP [9,20].

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Figure captions

- Fig. 1 Schematic picture of the relevant part of excess carrier excitation and recombination rates in PLE measurements via a deep acceptor level in n-type material. n_T and p_T denote the concentrations of occupied and empty electron states respectively. N_{TT} is the total concentration of the deep acceptor state.
- Fig. 2 Logarithmic plot of photoluminescence intensity for the A- and C-emissions vs excitation intensity for a few of the samples employed. A strictly linear behaviour is observed.
- Fig. 3 Schematic picture of the simple experimental setup used to record PLE-spectra for Zn-related acceptors in GaN. Monochromatic light from a double grating monochromator is focused on the sample, and the excited luminescence is detected with a S20 extended photomultiplier and recorded on a stripchart recorder as the excitation wavelength is scanned.
- Fig. 4 Schematic picture of optical excitations involving $\sigma_n^0(h\nu)$ for deep acceptor levels in GaN. Such transitions are those who mainly contribute to the measured absorption coefficient $\alpha(h\nu)$ in a transmission experiment.
- Fig. 5 Normalized optical cross sections $\sigma_n^0(h\nu)$ for Zn-doped GaN from PLE measurements with luminescence detection at $h\nu = 2.88$ eV (---), $h\nu = 2.53$ eV (—), and $h\nu = 2.38$ eV (·-·-·-) respectively. Note that a selective measurement of the $\sigma_{nA}^0(h\nu)$ cross section is only obtained with detection at $h\nu = 2.88$ eV in this case.

Fig. 6 Optical cross section $\sigma_{n_A}^0(h\nu)$, measured with PLE-technique at 4.2 K (—). Also included is a theoretical electronic spectrum $\sigma_{n_A,el}^0(h\nu)$, obtained by a deconvolution procedure employing a single linear mode model with $\hbar\omega_A = 74$ meV and $\lambda_A = 3$ (---).

Fig. 7 Normalized optical cross sections $\sigma_n^0(h\nu)$ for Zn-doped GaN obtained from PLE-spectra at 293 K with detection at two different photon energies. With the detection monochromator set at 2.88 eV only the $\sigma_{n_A}^0(h\nu)$ cross section is measured (—), while with detection at 2.69 eV an overlapping contribution from $\sigma_{n_B}^0(h\nu)$ is also clearly observed (---), since at this photon energy the B-emission is also detected, overlapping the low energy part of the A-emission.

Fig. 8 Spectral dependence of optical cross section $\sigma_{n_C}^0(h\nu)$ obtained from PLE-measurements at 4.2 K (—). Also shown is the calculated electronic curve $\sigma_{n_C,el}^0(h\nu)$, obtained from a deconvolution of the upper curve (—) with a linear single mode model, employing $\hbar\omega_C = 84$ meV and $\lambda_C = 3$.

Fig. 9 Collection of $\sigma_{n_A}^0(h\nu)$ curves at five different temperatures between 4.2 K (e) and 290 K (a), measured with PLE-technique and normalized at 3.35 eV. These curves show the experimental broadening behaviour of $\sigma_{n_A}^0(h\nu)$, but the horizontal position of the curves is influenced by the temperature shift of the A-level in the bandgap.

Fig. 10 Comparison between experimental broadening of $\sigma_{n_A}^0(h\nu)$ at 293 K, curve b (— — —), and theoretical broadening obtained by a convolution procedure, employing a linear one-phonon model ($\hbar\omega_A = 74$ meV, $\lambda = 3$, curve d) and a linear two-phonon model ($\hbar\omega_{A1} = 74$ meV, $\lambda_{A1} = 2.8$; $\hbar\omega_{A2} = 20$ meV, $\lambda_{A2} = 2$) respectively. Curve e is the experimental optical cross section $\sigma_{n_A}^0(h\nu)$ at 4.2 K, curve a the corresponding curve at 293 K. Curve b is obtained from curve a by a rigid shift of 15 meV towards higher energy, to compensate for the independently deduced shift of the A-level with temperature [7]. All curves are normalized at about 3.35 eV.

Fig. 11 Normalized optical cross sections $\sigma_{n_C}^0(h\nu)$, obtained with PLE-technique at 4.2 K (curve d) and 293 K (curve a). Also shown is a comparison between experimental broadening of $\sigma_{n_C}^0(h\nu)$ at 293 K (curve b) and theoretical broadening at 293 K as obtained from a simple linear one-phonon model with $\hbar\omega_C = 84$ meV, $\lambda_C = 3$ (curve c). Curve b is obtained from curve a by a rigid shift of 30 meV towards higher photon energy, to compensate for the temperature shift of the C-level up to 293 K [7]. Introduction of a second phonon mode is expected to improve the agreement between curves b and c (cf. Fig. 10).

Fig. 12 Spectral behaviour of absorption coefficient $\alpha(h\nu)$ at 77 K for a Zn-doped GaN-layer of 50 μm thickness. A background absorption of about 300 cm^{-1} seems to be present, from the behaviour below 2.0 eV. The sharp rise at 3.1–3.2 eV is due to the $\sigma_{n_A}^0(h\nu)$ cross section. Approximate contributions from cross sections associated with levels B, C, and D are also indicated.

Fig. 13 Comparison between normalized optical transition matrix elements for the Zn-related A-centre in GaN, in emission ($\frac{I(\nu)}{\nu^3}$, curve a) and absorption ($\frac{\sigma(\nu)}{\nu}$, curve b). Curve c is identical to curve a, mirrored in the cross-over point between curves a and b. The different spectral shape of curves b and c supports the idea that b is related to an optical cross section. The cross-over point between curves a and b is a good estimate of the position of the unperturbed electronic A-level (around 3.16 eV from the conduction band edge).

Fig. 14 Similar curves as in Fig. 13 for the Zn-related C-level in GaN. Curve a denotes optical matrix element for the C-emission ($\frac{I(\nu)}{\nu^3}$), curve b the same in absorption ($\frac{\sigma(\nu)}{\nu}$), while curve c is identical to curve a, if mirrored at the cross-over point (2.48 eV). The obvious difference in spectral shape between curves b and c supports the idea that the measured PLE-curves (Figs. 8 and 11) are really optical cross sections $\sigma_{nC}^0(h\nu)$.

Fig. 15 Schematic configuration coordinate model for optical transitions via a localised impurity state, with a single-mode linear interaction involving a quasilocalized vibration (left). The corresponding optical excitations in the band diagram is also shown (right). Zero-phonon (electronic) transitions are shown (—), together with Stokes components involved in the main optical lineshape (— — —). Anti-Stokes components of vibronic transitions causing temperature broadening are also indicated (— • — • — •).

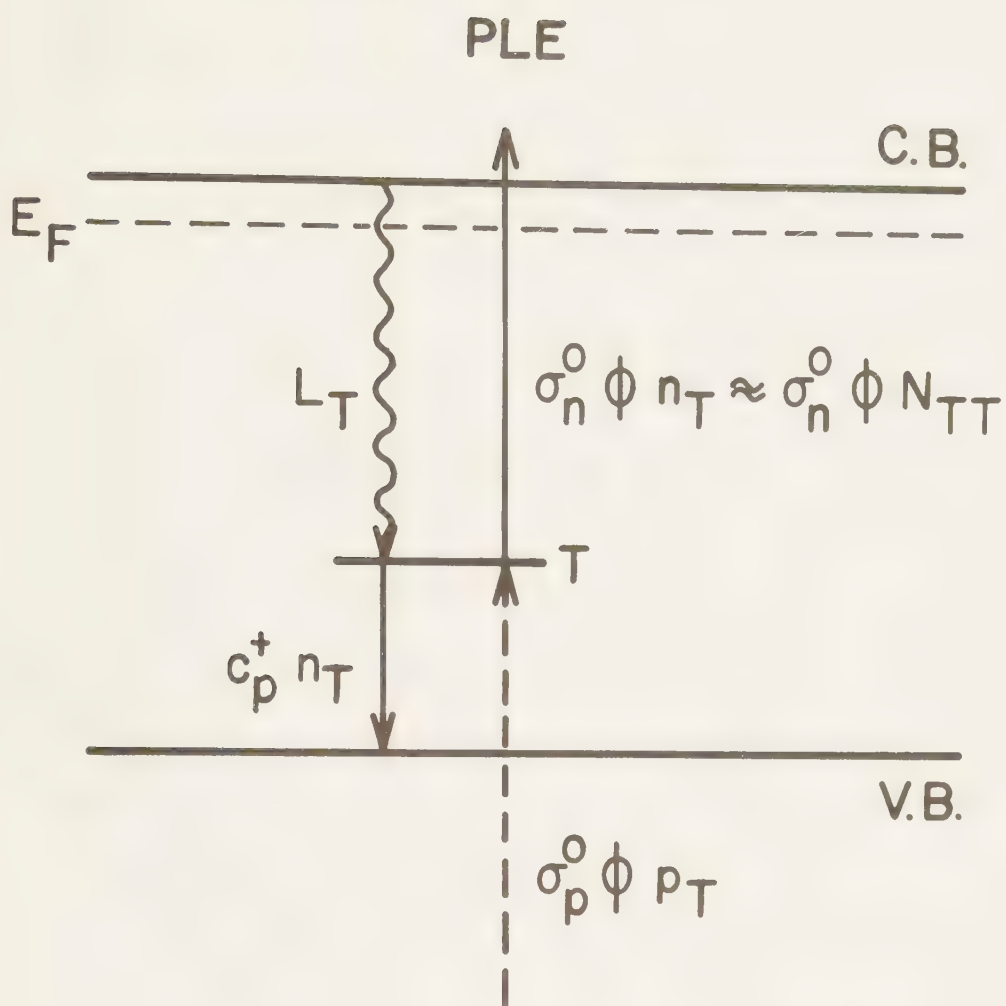
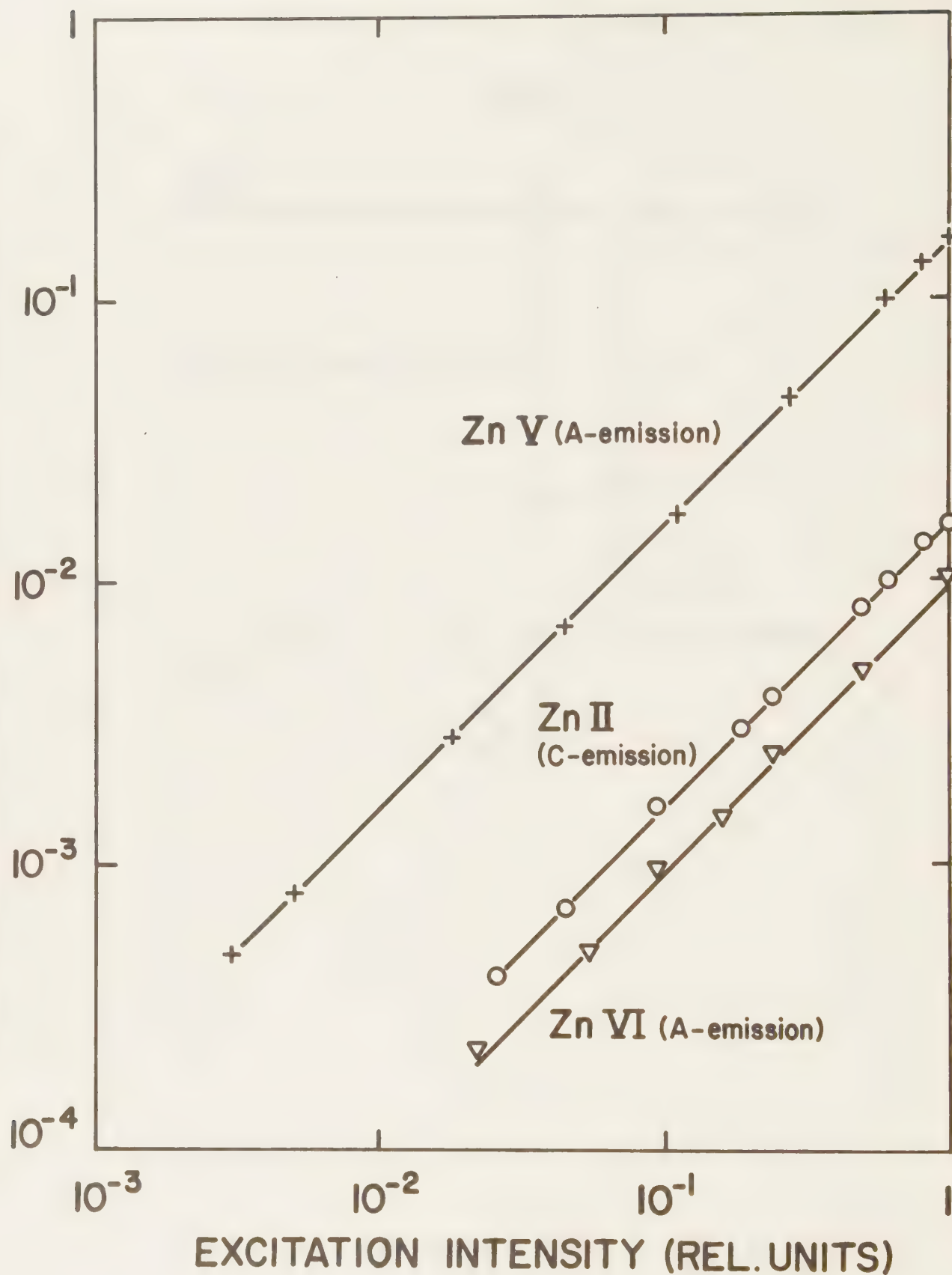


Fig. 1

PHOTOLUMINESCENCE INTENSITY (REL. UNITS)



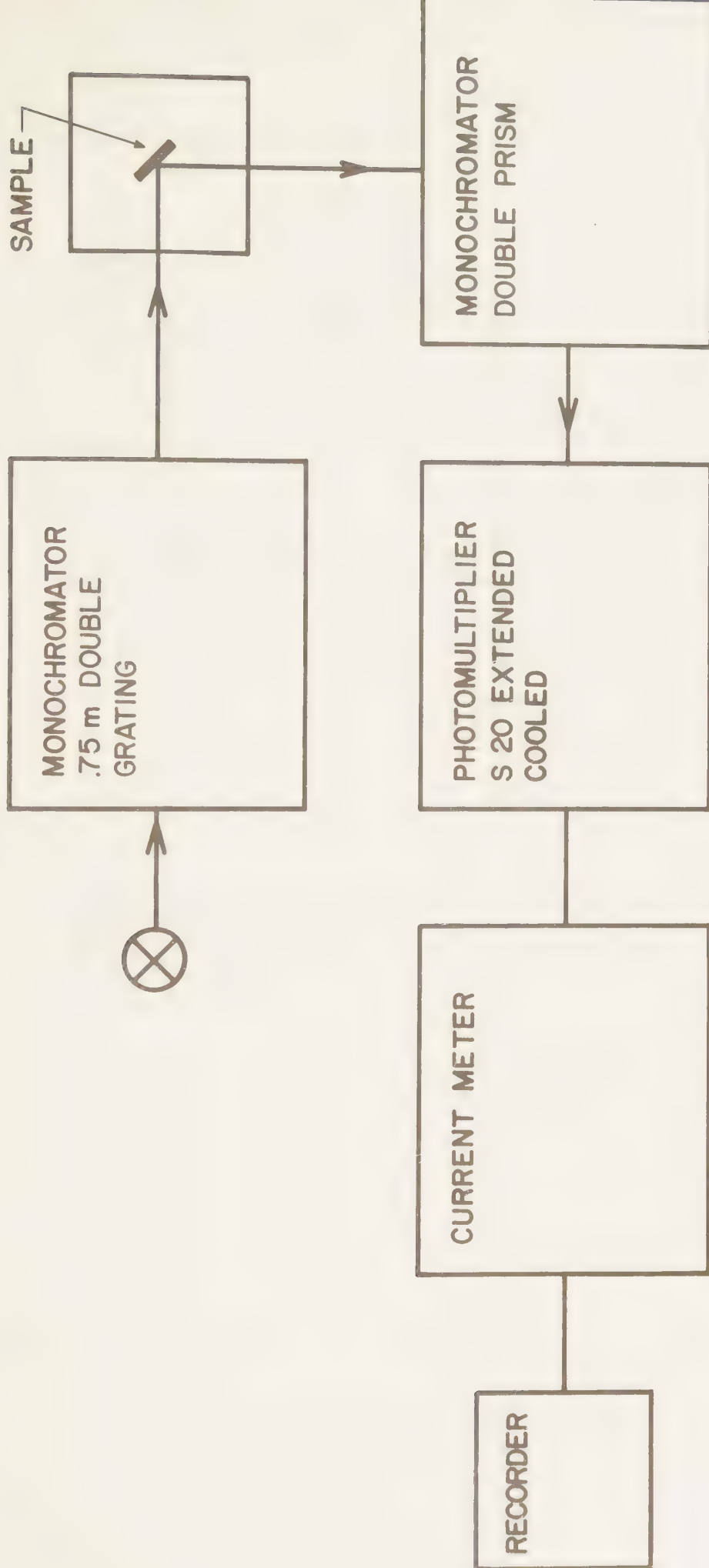


Fig. 3

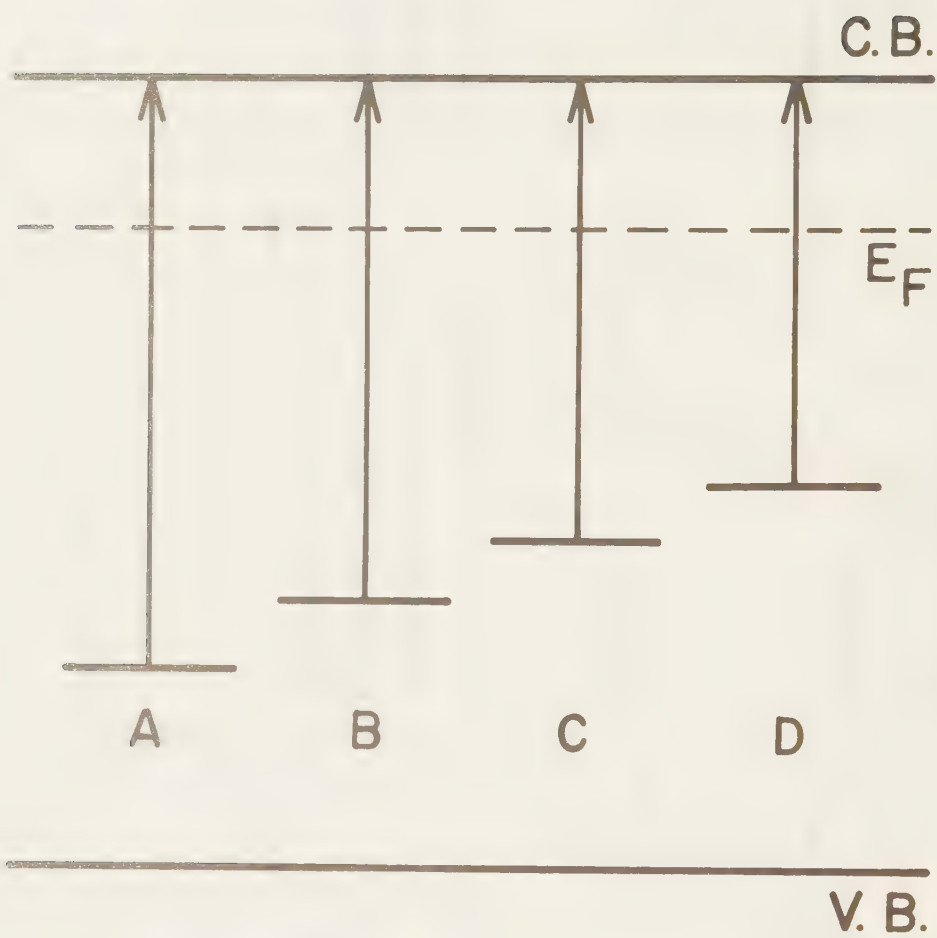


Fig. 4

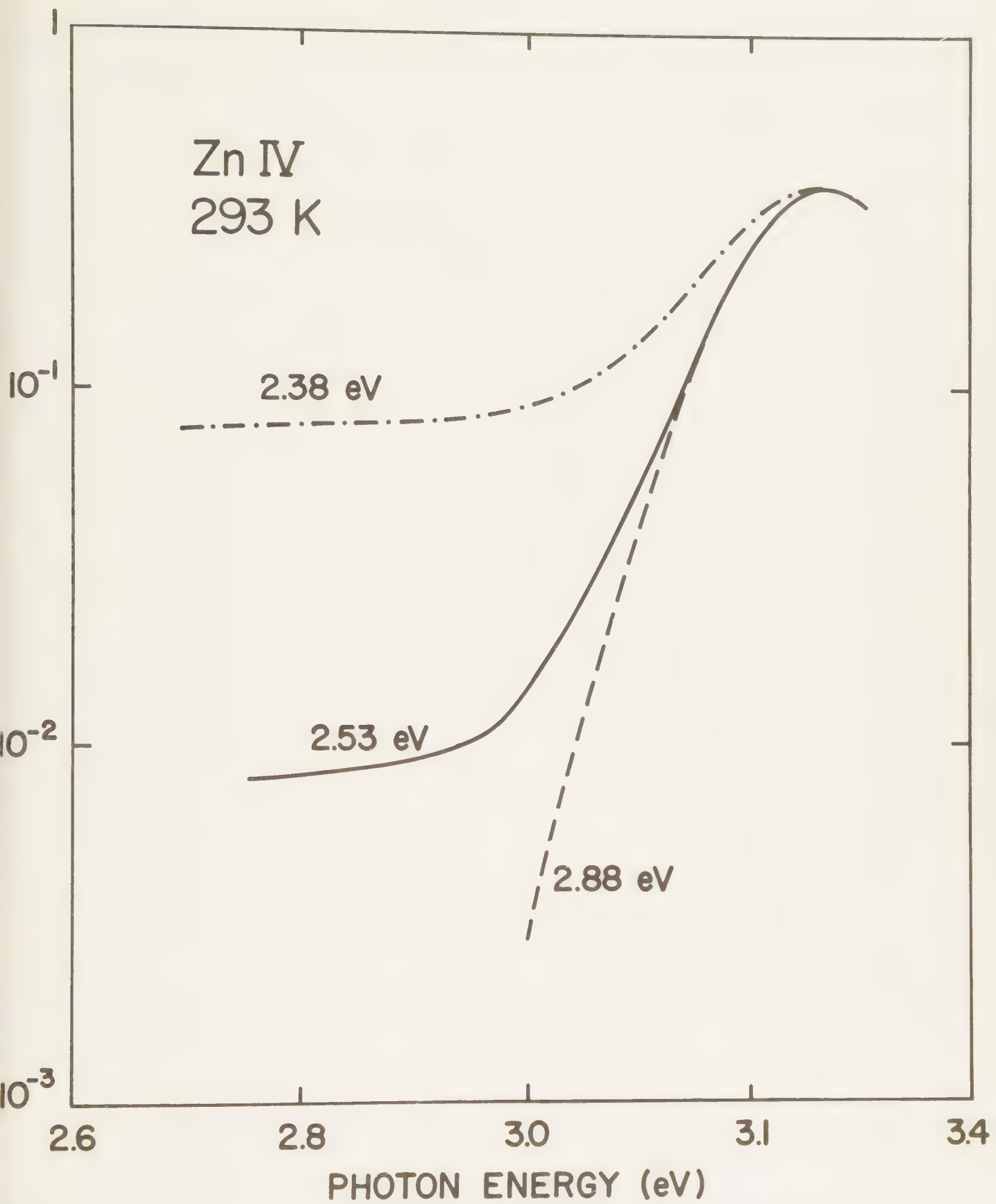


Fig. 5

CROSS SECTION (ARB. UNITS)

Zn VI
4.2 K

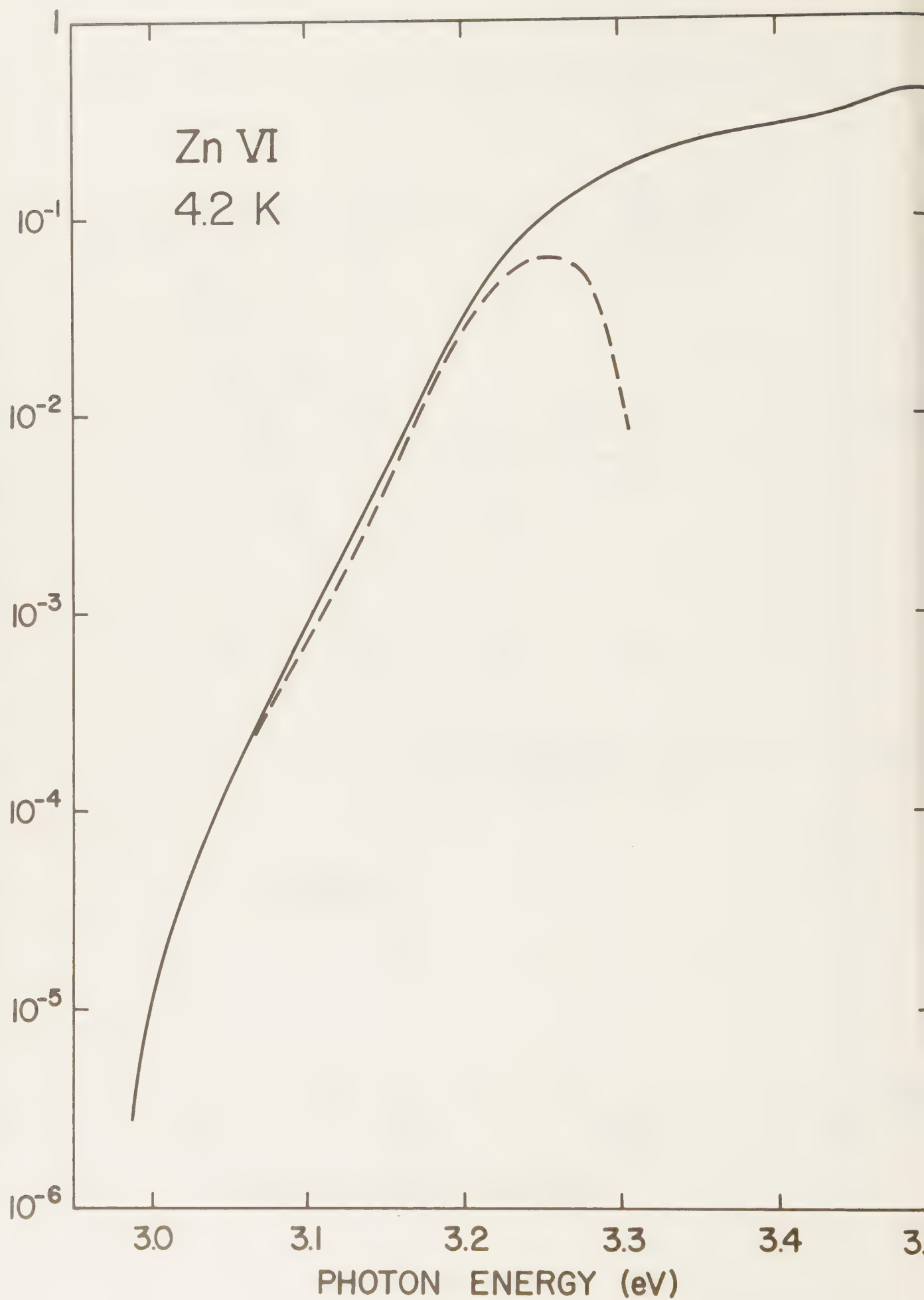


Fig.

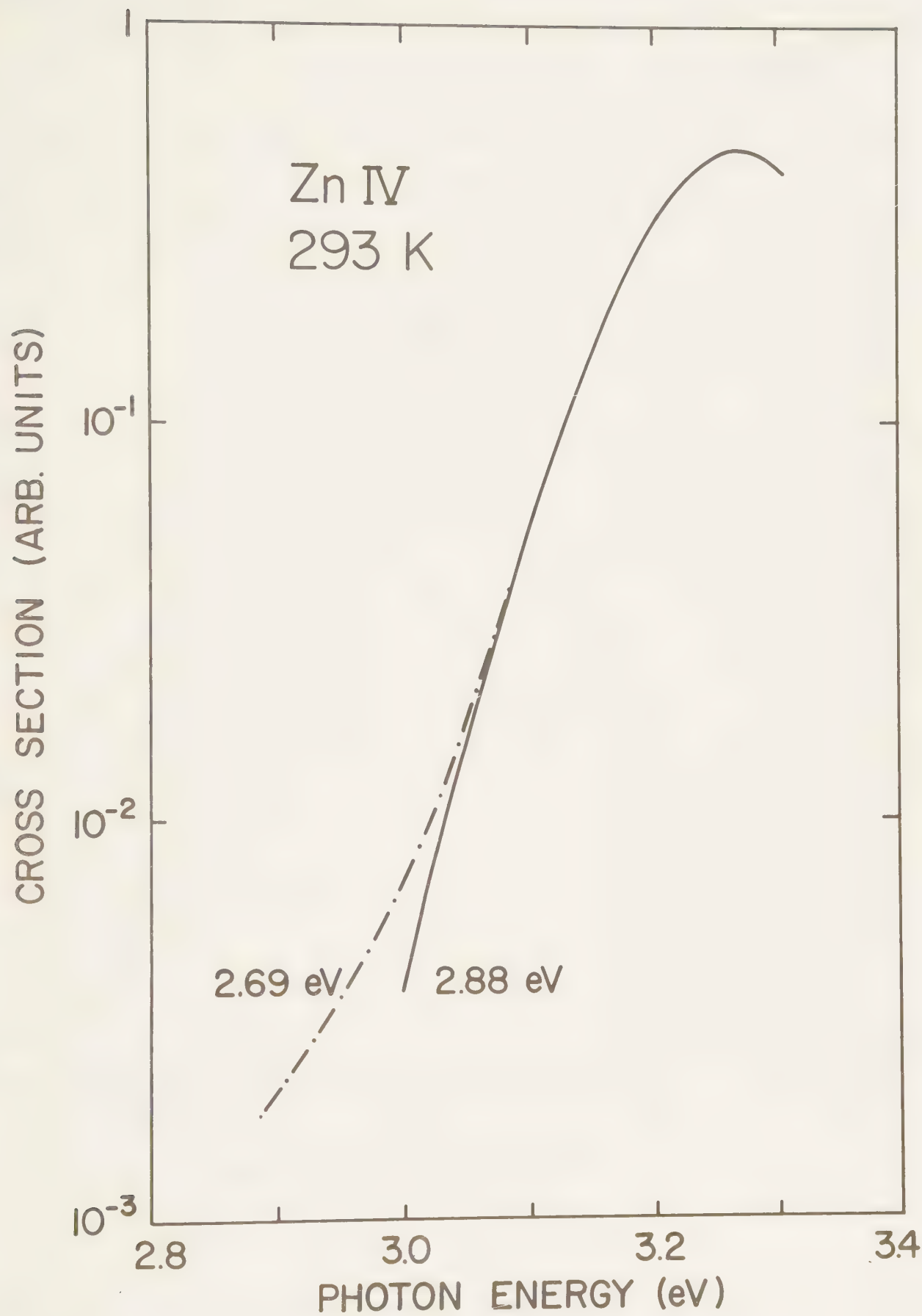
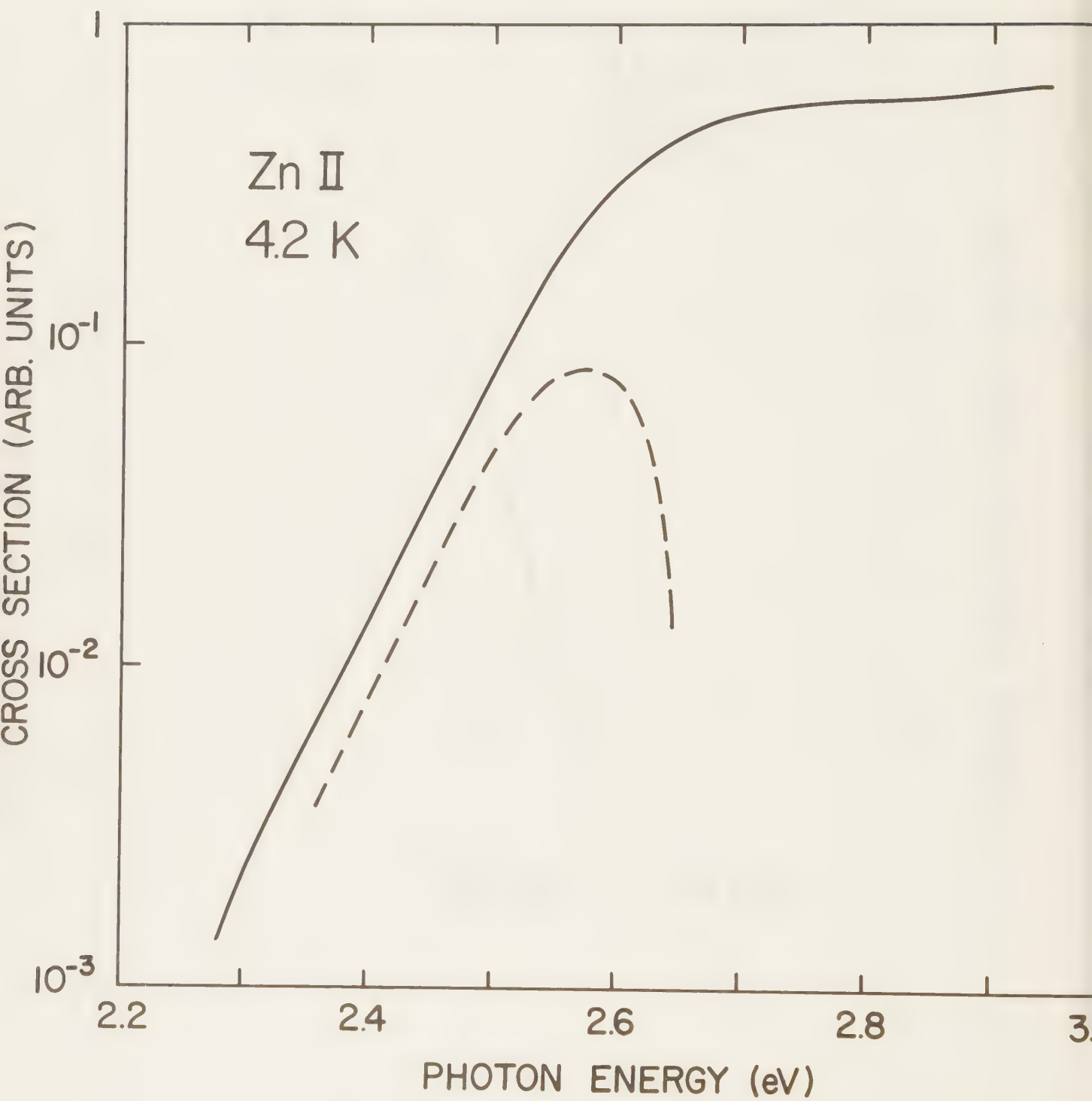


Fig. 7



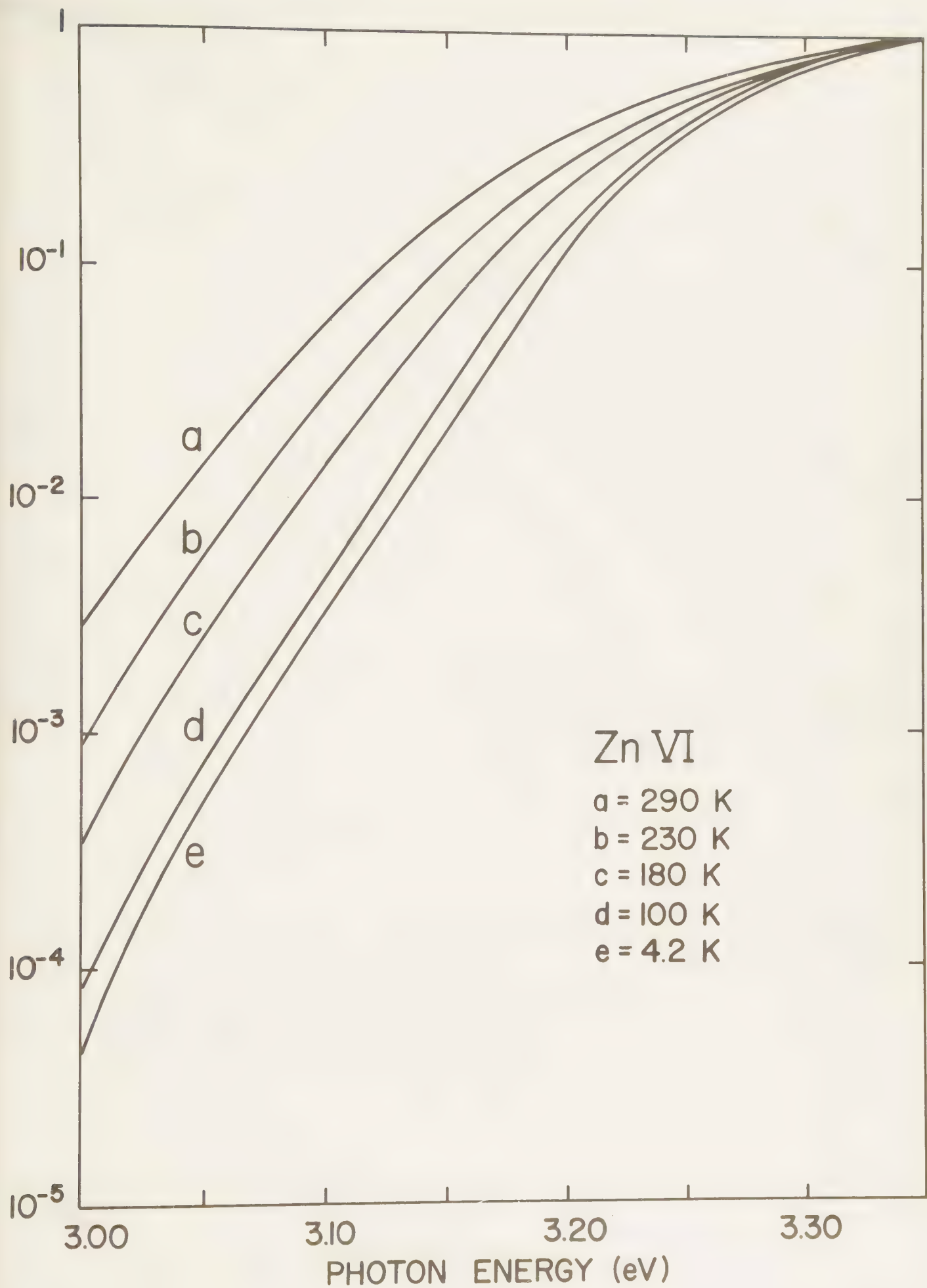


Fig. 9

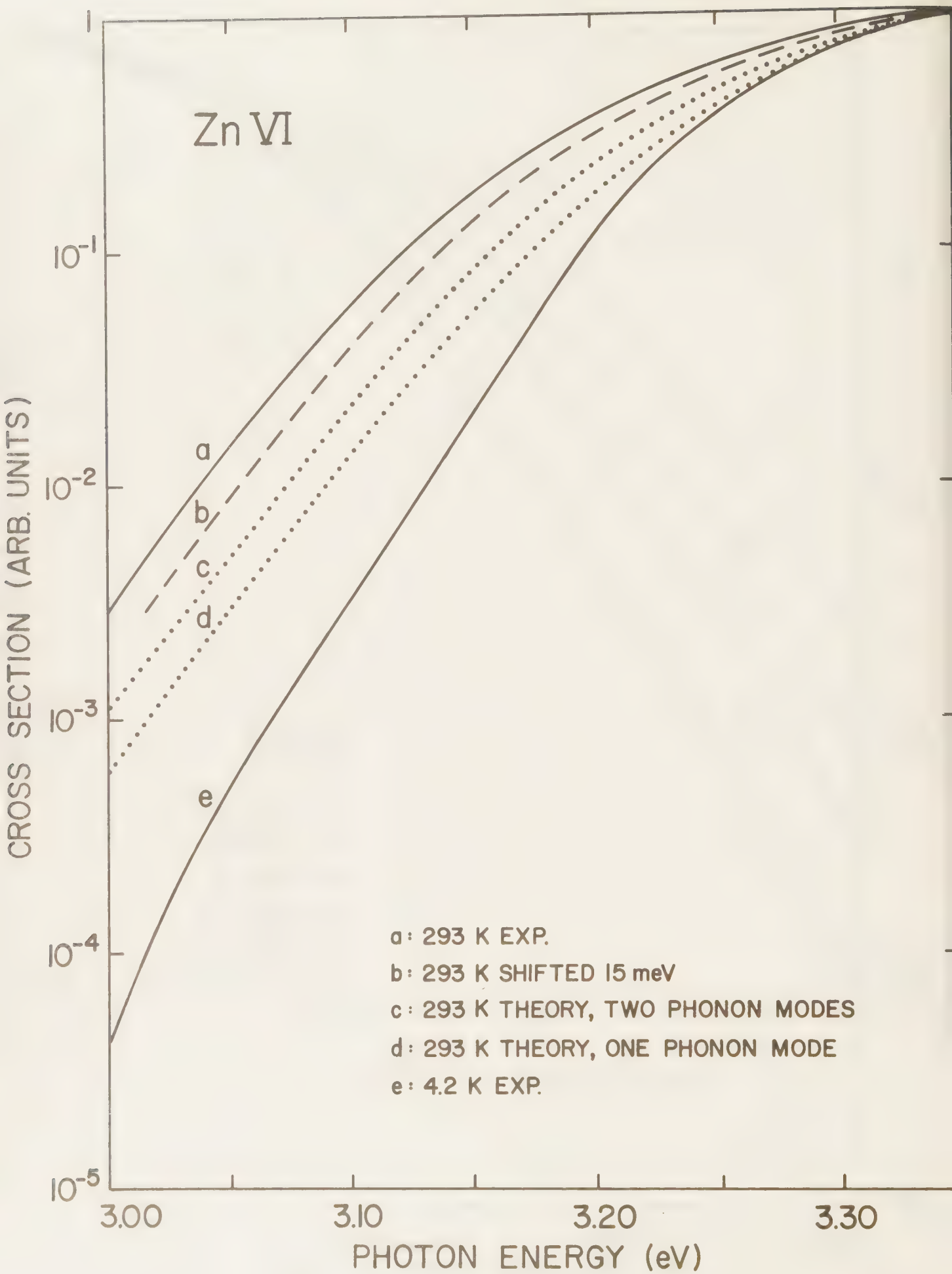


Fig.

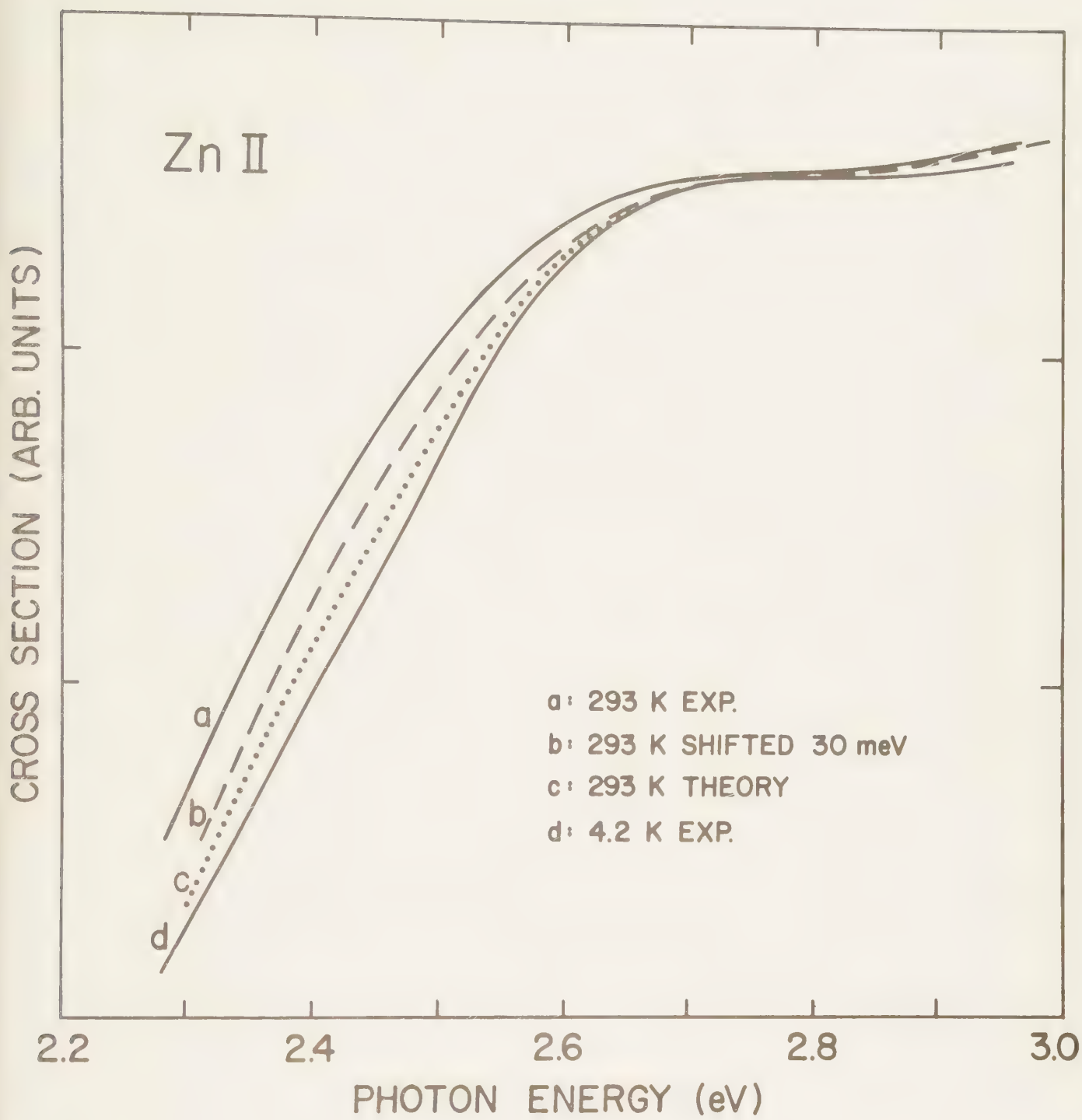
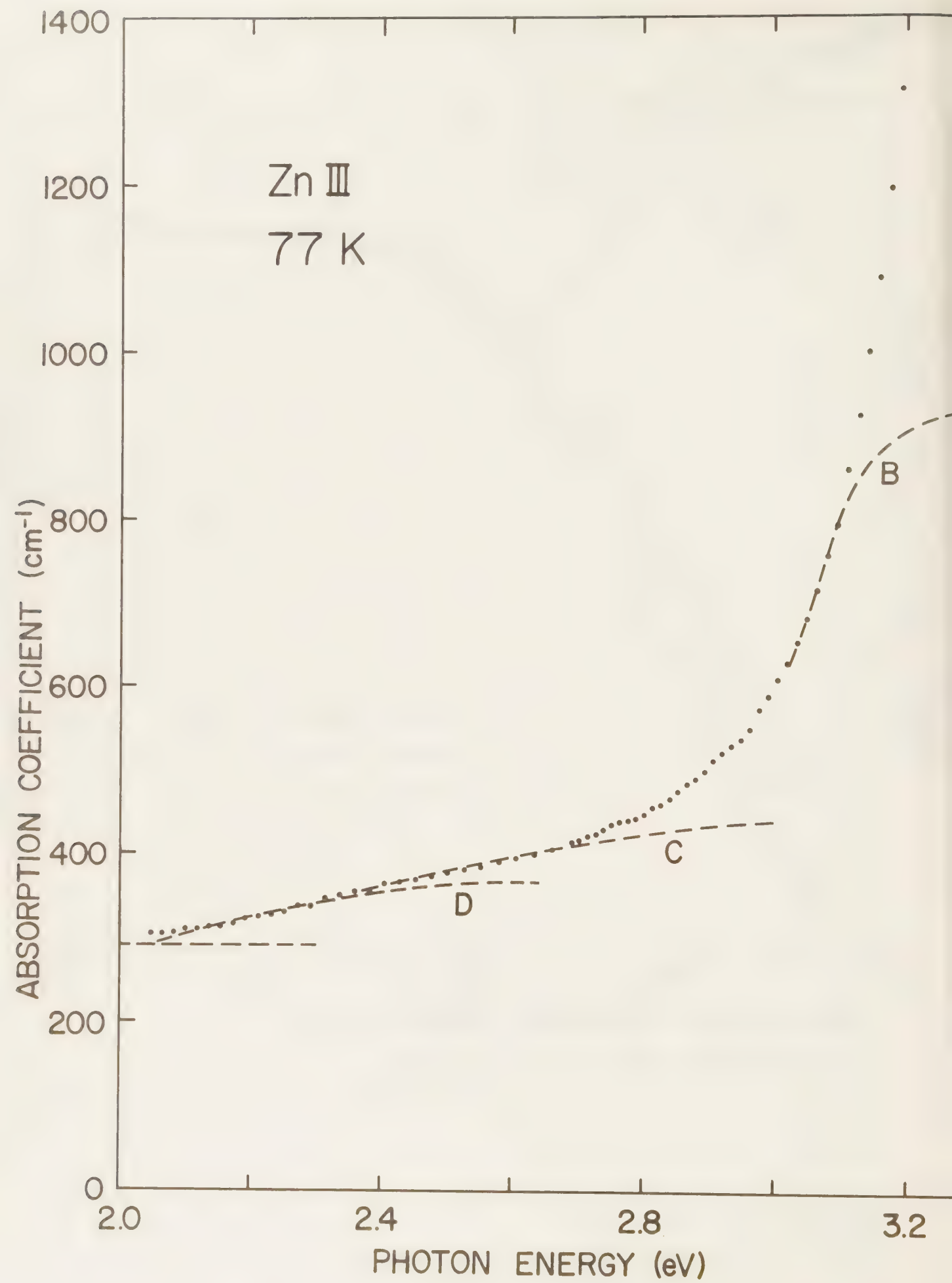


Fig. 11



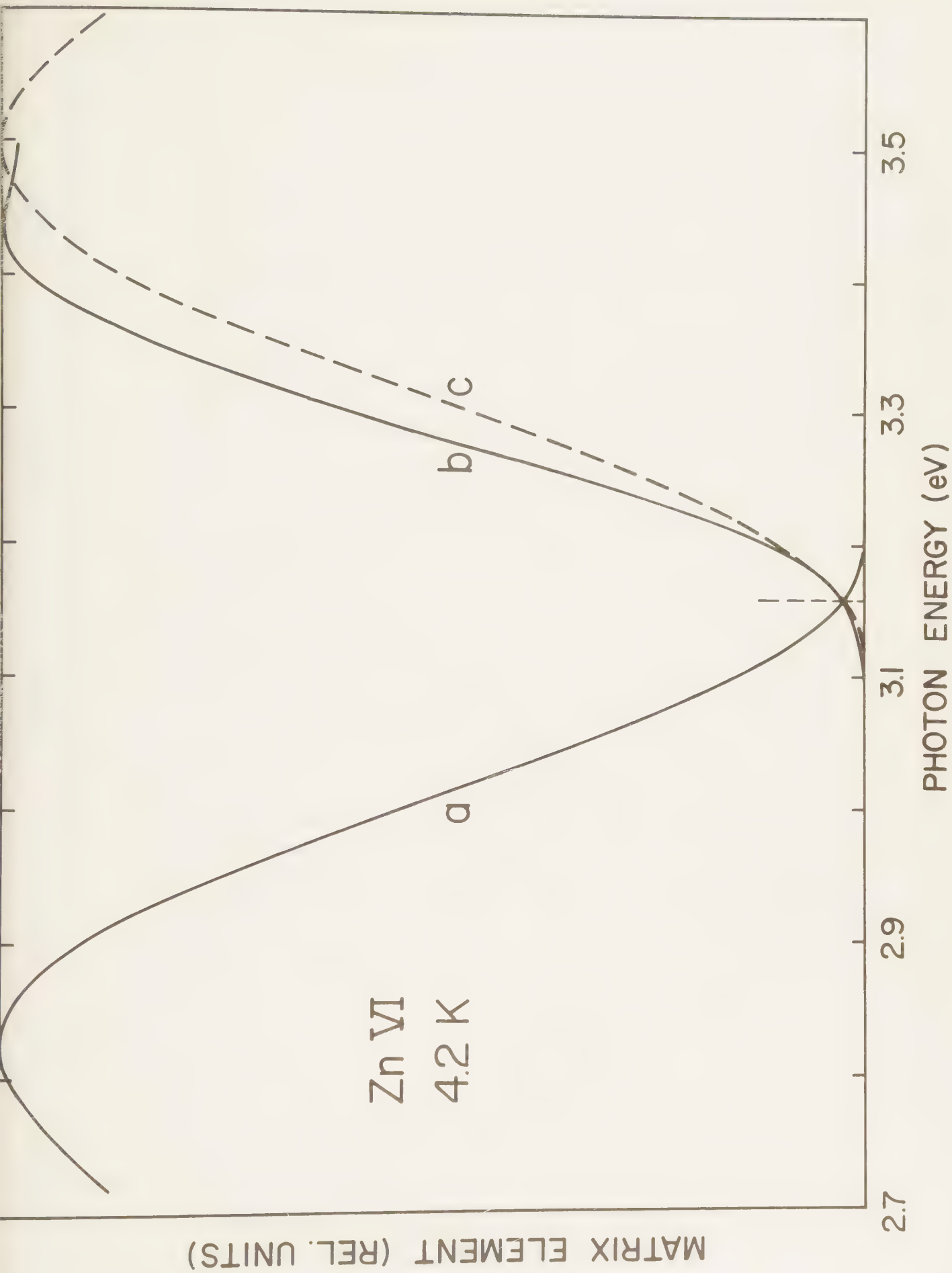
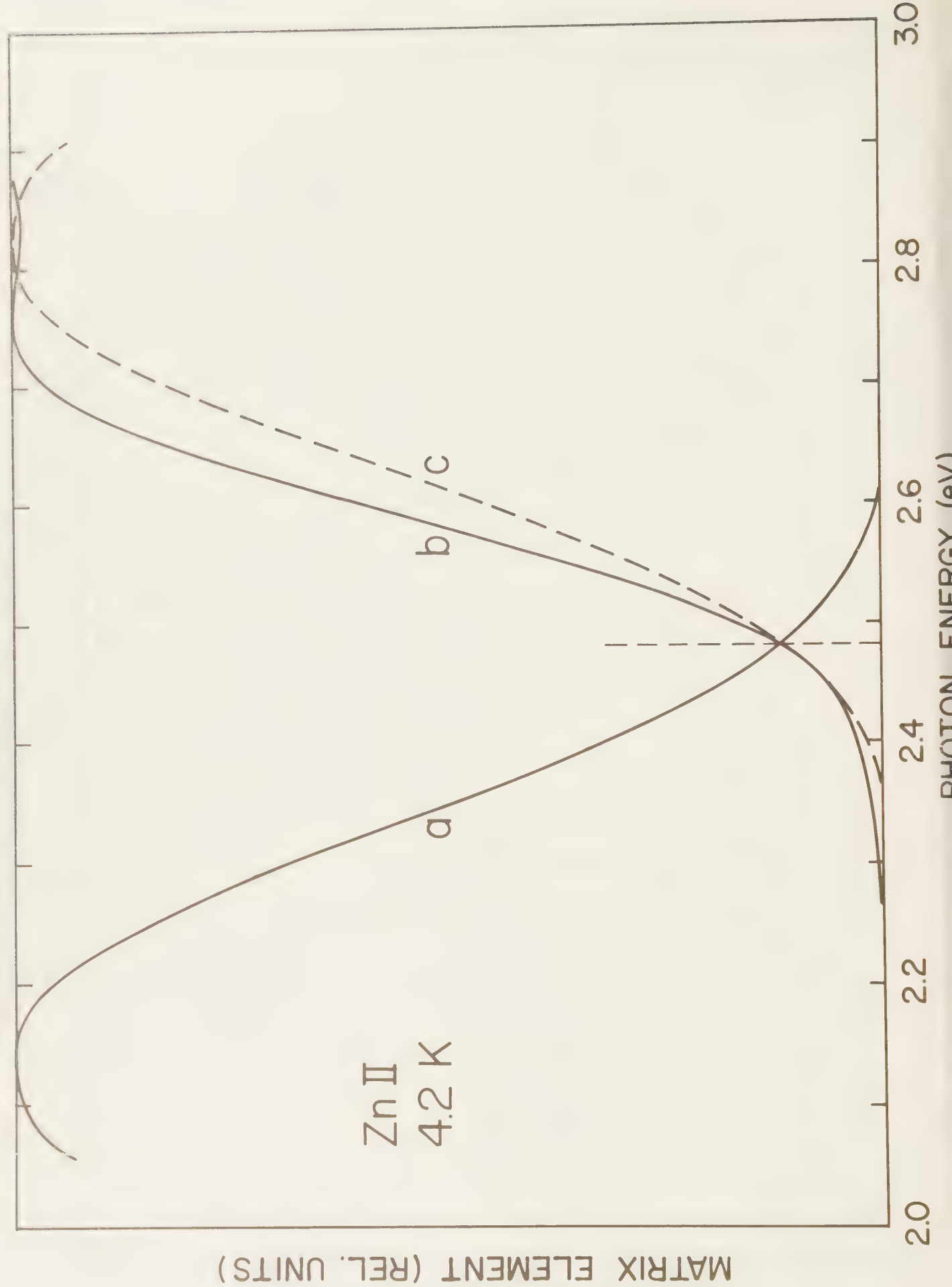


Fig. 13



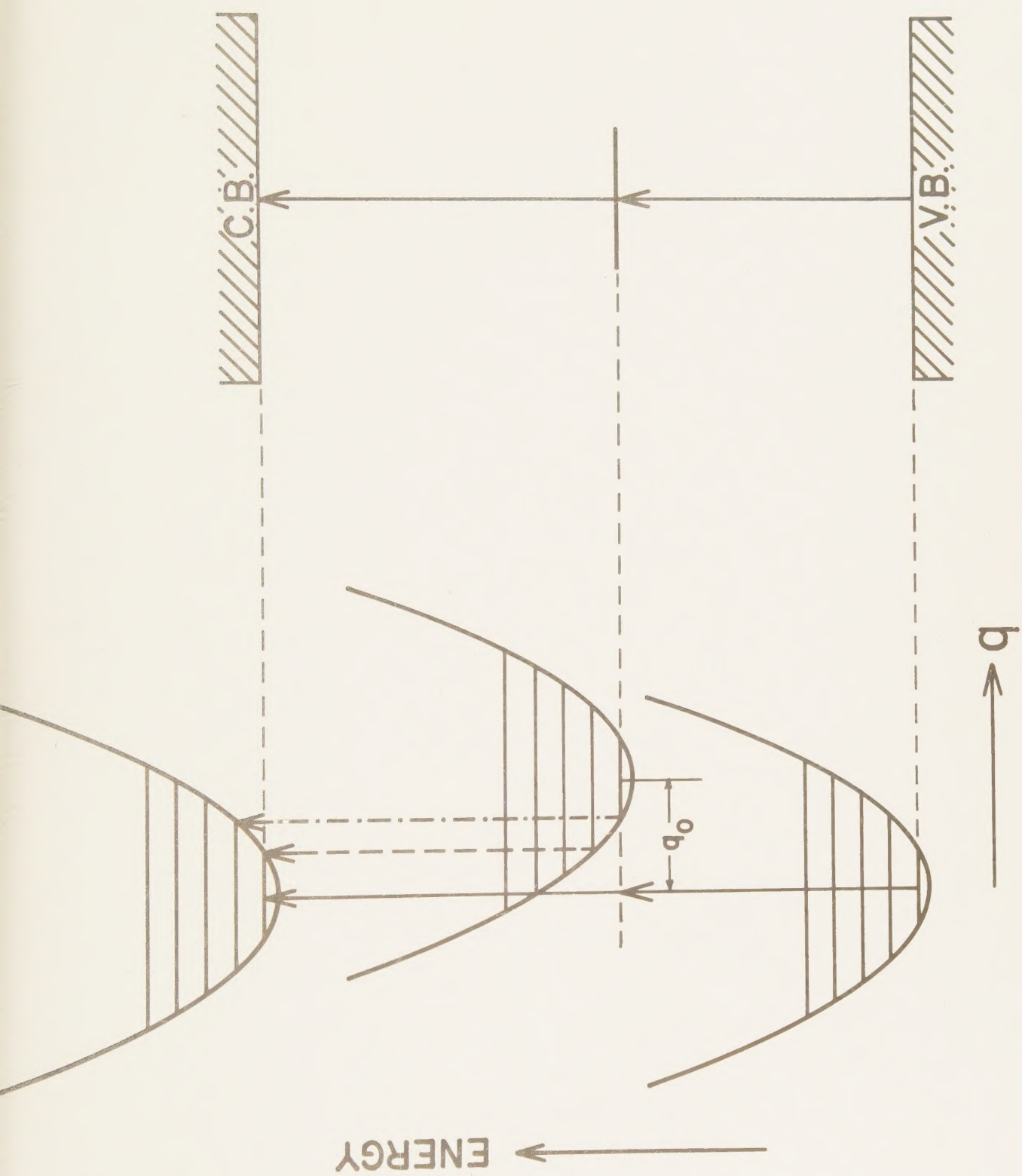


Fig. 15

